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$CoTeMoO_6$, $Co_4TeMo_3O_{16}$: Two New Cobalt Molybdotellurates

R. KOZŁOWSKI AND J. SŁOCZYŃSKI

Research Laboratories of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Krupnicza 41, 30–060 Kraków, Poland

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It has been found that a solid-state reaction of $CoMoO_4$ with TeO_2 at 500°C yields a new compound of the formula $CoTeMoO_6$. This compound is also formed in the course of annealing of $CoMoO_4$–H_6TeO_6 mixtures. Another new compound, the cobalt molybdotellurate containing Te^{6+}, was prepared by a solid-state reaction of Co_5TeO_8 with MoO_3. It has the formula $Co_4TeMo_3O_{16}$. Both $CoTeMoO_6$ and $Co_4TeMo_3O_{16}$ have been characterized by X-ray method. The latter has the structure of a wolframite type with the unit cell dimensions $a = 4.66$, $b = 5.67$, $c = 4.96$ Å, $\beta \simeq 90°$.

Introduction

The present paper is concerned with phase and structural investigations of the products formed in the course of solid-state reactions between $CoMoO_4$ and tellurium oxides. The system Co–Te–Mo–O has been reported to catalyze allylic oxidation of olefins to unsaturated carboxylic acids, in particular oxidation of propylene to acrylic acid (*1–3*). The phase composition of catalysts in the Co–Te–Mo–O system, however, has not been fully explained so far. It seemed of interest to study what compounds of definite formula (if any) exist in this system. At the same time the cobalt salts of the well-known molybdotelluric acids, $H_8TeMo_6O_{24}$ and $H_6TeMo_6O_{24}$, were prepared and the products of their thermal decomposition were investigated. The results obtained have been published elsewhere (*4*).

Experimental

The materials used in the preparation were: $CoMoO_4 \cdot H_2O$, obtained by precipitation from solution according to the method described in (*5*); TeO_2 and H_6TeO_6, both commercial products of chemically pure grade. The appropriate amounts of reagents were mixed with small amounts of water, homogenized, and dried. The reaction mixtures were calcined in air at the desired temperatures cooled afterwards to room temperature, and ground.

After dissolution in cold or hot concentrated HCl the samples were analyzed in the following way: Tellurium was determined colorimetrically in the form of colloidal Te obtained by reduction of Te^{4+} and Te^{6+} with stannous chloride, as well as with the weight method in the form of elemental Te. In order to determine separately Te^{4+} and Te^{6+} contents, the Bunsen–Rupp method was applied (*6*). Cobalt was determined colorimetrically, in a 1:1 acetone–water solution using thiocyanate method. Molybdenum was determined colorimetrically in the form of the phenylhydrazine complex in an acidic medium.

Dta and Tg curves were obtained with aid of Paulik–Paulik–Erdey apparatus in air with heating rate of 5°/min.

X-ray powder patterns were obtained with a DRON-1 diffractometer using Cu*Kα* radiation.

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Results

1. $Co_4TeMo_3O_{16}$

In the course of the preparation of active catalysts for formation of acrylic acid in oxidation of propylene, small amounts of TeO_2 (2–7 wt%) were added during precipitation of $CoMoO_4 \cdot H_2O$. The precipitates with different amounts of TeO_2 were then heated for several hours at temperatures between 380 and 600°C. The obtained samples, in the course of dissolution in cold concentrated HCl, revealed the presence of small amounts of insoluble phase. The chemical analysis of this compound, performed after its dissolution in hot concentrated HCl, showed that its composition corresponded to the formula, $Co_4TeMo_3O_{16}$, which can be formally derived from $CoMoO_4$ by replacing every fourth Mo^{6+} ion by Te^{6+}. The results of the chemical analysis are shown in Table I.

It appeared, however, that $Co_4TeMo_3O_{16}$ was not merely a solid solution of $CoMoO_4$ and hypothetical $CoTeO_4$ since the new phase composition was independent of the $CoMoO_4$: TeO_2 ratio in the initial mixtures and the annealing temperature.

The attempts to prepare $Co_4TeMo_3O_{16}$ in larger quantities were then undertaken. When, however, $CoMoO_4$–H_6TeO_6 mixtures were calcined at 550°C, a compound containing tetravalent tellurium was formed. This indicates that the solid-state reaction to $Co_4TeMo_3O_{16}$ occurs at the temperature higher than that of the $H_6TeO_6 \rightarrow TeO_2$ decomposition (H_6TeO_6 decomposes at 220°C to TeO_3 which transforms to TeO_2 at 395°C).

In view of this fact, another Te^{6+} containing reactant, thermally stable up to 500°C, had to be used. The cobalt tellurate of spinel type, Co_5TeO_8, reported by Kasper (7), stable over the temperature range 25–1200°C, has been chosen. It was obtained according to the method described in the quoted paper. Co_5TeO_8 was mixed with the appropriate quantity of MoO_3 according to the following exchange reaction:

$$Co_5TeO_8 + 4MoO_3 \rightarrow Co_4TeMo_3O_{16} + CoMoO_4.$$

The reaction mixture was heated for 24 hr at 550°C. The X-ray diffraction pattern of the product obtained revealed the presence of only $Co_4TeMo_3O_{16}$ and $CoMoO_4$. Pure $Co_4TeMo_3O_{16}$ was obtained by subsequent washing of the reaction product with concentrated NH_3, cold concentrated HCl, and water in order to remove the starting reactants and $CoMoO_4$. The sample so prepared gave an X-ray pattern showing no lines attributable to unreacted material or $CoMoO_4$. The

TABLE I

ANALYSIS OF $Co_4TeMo_3O_{16}$

	% CoO	% TeO_3	% MoO_3	Co:Te:Mo ratio
Found	33.6	19.8	47.1	4.00:1.00:2.92
Calculated	33.0	19.4	47.6	4:1:3

TABLE II

X-RAY POWDER DATA FOR $Co_4TeMo_3O_{16}$ (WOLFRAMITE TYPE, $a = 4.66$, $b = 5.67$, $c = 4.96$ Å, $\beta \simeq 90°$)

$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}
0 1 0	5.70	5.68	3	2
1 0 0	4.67	4.66	12	10
0 1 1	3.74	3.73	12	11
1 1 0	3.61	3.60	27	26
1 1 1	2.916	2.913	100	100
0 2 0	2.838	2.842	12	10
0 0 2	2.483	2.478	14	15
0 2 1	2.465	2.465	14	13
2 0 0	2.330	2.328	6	7
1 0 2	2.195	2.190	7	9
1 2 1	2.176	2.178	10	10
1 1 2	2.039	2.041	10	8
2 1 1	1.974	1.975	2	1
0 2 2	1.869	1.867	15	7
2 2 0	1.800	1.801	7	6
1 3 0	1.752	1.755	16	13
2 0 2	1.693	1.698	42	35
2 2 1		1.691		
0 3 2	1.503	1.505	20	18
1 1 3		1.501		
3 1 0		1.497		
0 2 3	1.429	1.428	32	28
1 3 2		1.432		
3 1 1		1.433		

chemical analysis confirmed the suggested composition of $Co_4TeMo_3O_{16}$.

The powder pattern of $Co_4TeMo_3O_{16}$ shown in Table II displays the arrangement of lines typical for a wolframite structure type. The unit cell dimensions calculated from this pattern are: $a = 4.66$, $b = 5.67$, $c = 4.96$ Å, $\beta \simeq 90°$. The absence of the superlattice reflections indicates random distribution of Te and Mo atoms over the lattice positions of six-valent metal ions (M^{6+}) in a structure of wolframite type. The reflection intensities were calculated using the coordinates of atoms in a wolframite structure type given by Ülkü for $FeWO_4$ (*8*) and assuming the random distribution of Te and Mo atoms over the M^{6+} positions. The comparison of observed and calculated intensities (Table II) shows reasonable agreement, confirming the suggested structure model.

The Dta curve of $Co_4TeMo_3O_{16}$ shows a single endothermal effect at 740°C accompanied by a weight loss of 1.6 %. These effects correspond to the melting of $Co_4TeMo_3O_{16}$. The X-ray examination and chemical analysis of cooled melt indicate that $Co_4TeMo_3O_{16}$ melts incongruently, decomposing to $CoMoO_4$, and that Te^{6+} in liquid simultaneously reduces to Te^{4+}.

2. *CoTeMoO₆*

The $CoMoO_4$–TeO_2 oxide system was investigated by the X-ray method in order to check compound formation. The composition of investigated samples varied from pure $CoMoO_4$ to pure TeO_2. The reaction mixtures were calcined in air at 300°C for 12 hr and then, after cooling to room temperature and grinding, at 550°C for 12 hr. The results of X-ray analysis indicate that only one compound, of the composition $CoMoO_4 \cdot TeO_2$ ($CoTeMoO_6$) is formed. In the composition range $CoMoO_4$–$CoMoO_4 \cdot TeO_2$, the supercooled high-temperature modification of $CoMoO_4$ and the compound $CoTeMoO_6$ have been detected. With the increasing TeO_2 content, the line intensities of $CoMoO_4$ decrease until complete disappearance at the $CoMoO_4{:}TeO_2 = 1{:}1$ molar ratio. In the composition range $CoMoO_4 \cdot TeO_2$–TeO_2 the compound coexists with pure TeO_2. In order to confirm the suggested composition of the compound, the X-ray microanalysis of the calcined $CoMoO_4$–TeO_2 mixtures was carried out (*9*). The homogenous well-defined crystals of the suggested $CoO{:}TeO_2{:}MoO_3 = 1{:}1{:}1$ composition were found in the investigated samples, confirming the assumed composition, $CoTeMoO_6$, of a new phase.

The absence of $Co_4TeMo_3O_{16}$ among the reaction products indicates that this compound is not formed by two-step calcination of the $CoMoO_4 \cdot H_2O$–TeO_2 mixtures at 300 and 550°C. The formation of small amounts of $Co_4TeMo_3O_{16}$ in the first experiments seems to have been caused by the presence of residual undecomposed TeO_3 at the temperature of the solid-state reaction.

TABLE III

$CoTeMoO_6$ X-RAY PATTERN

d(Å)	I^a
8.84	vw
4.43	s
3.65	s
3.38	m
3.33	m
3.12	vw
2.912	vw
2.814	vs
2.628	w
2.531	w
2.300	vw
2.257	w
2.218	vw
2.200	vw
1.963	vw_b
1.921	vw
1.822	m
1.804	vw
1.688	w_b
1.669	w_b
1.609	vw
1.589	vw_b
1.550	w
1.509	w

[a] v, very; s, strong; m, middle; w, weak; b, broad.

TABLE IV

CRYSTALOCHEMICAL DATA FOR $A\mathrm{MoO_4}$-TYPE COMPOUNDS

Compound	Structure type	Coordination		Reference
		A^{2+}	Mo^{6+}	
$\mathrm{MgMoO_4}$[a]	Wolframite	6	6	*10, 11*
$\mathrm{NiMoO_4}$[a]		6	6	*10, 11*
$\mathrm{CoMoO_4}$[a]		6	6	*10, 11*
$\mathrm{FeMoO_4}$[a]		6	6	*10, 11*
$\mathrm{MnMoO_4}$[a]		6	6	*10, 11*
$\mathrm{ZnMoO_4}$[a]		6	6	*10, 11*
$\mathrm{ZnMoO_4}$		6	6	*12*
$\mathrm{CoMo_{3/4}Te_{1/4}O_4}$		6	6 (Mo, Te)	Present work
$\mathrm{CdMoO_4}$	Scheelite	8	4	*13*
$\mathrm{CaMoO_4}$		8	4	*13*
$\mathrm{SrMoO_4}$		8	4	*13*
$\mathrm{BaMoO_4}$		8	4	*13*
$\mathrm{PbMoO_4}$		8	4	*13*
$\mathrm{MnMoO_4}$	*a* ($\mathrm{MnMoO_4}$)	6	4	*14*
$\mathrm{MgMoO_4}$	*a*	6	4	*15*
$\mathrm{CoMoO_4}$[b]	*b* ($\mathrm{CoMoO_4}$)	6	6	*16*
$\mathrm{NiMoO_4}$[b]	*b*	6	6	*16*
$\mathrm{FeMoO_4}$[b]	*b*	6	6	*11*
$\mathrm{CuMoO_4}$	$\mathrm{CuMoO_4}$	6, 5	4	*17*
$\mathrm{ZnMoO_4}$	$\mathrm{ZnMoO_4}$	6, 5	4	*18*

[a] Prepared at high pressure (60 kbars).

[b] These compounds have the high-temperature modifications of *a* type.

The X-ray powder data for $\mathrm{CoTeMoO_6}$ are given in Table III. There are no structural data for this compound so far.

The Dta and X-ray examinations indicate that $\mathrm{CoTeMoO_6}$ melts incongruently at 651 °C, decomposing in this process to $\mathrm{CoMoO_4}$.

Conclusions

The divalent metal molybdates of the general formula $A\mathrm{MoO_4}$ crystallize in several different structure types, as shown in the Table IV. As seen from Table IV, only the high-pressure modifications of the molybdates of the small cations adopt the wolframite structure characteristic of the corresponding normal-pressure tungstates (*10*). The only case of the molybdate with the wolframite structure type obtained at ambient pressure is $\mathrm{ZnMoO_4}$ (*12*).

It has been shown in the present work that the partial substitution of Mo atoms in $\mathrm{CoMoO_4}$ by Te atoms results in transformation to the wolframite type structure. The doublet: $\mathrm{Co_4TeMo_3O_{16}}$–high-pressure $\mathrm{CoMoO_4}$, in addition to the doublet $\mathrm{CoWO_4}$–high-pressure $\mathrm{CoMoO_4}$, is an example of high-pressure oxide of the same structure type as that of the ambient pressure oxide with cations substituted by another element from the same periodic group.

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