PHASE RELATIONS IN THE $CoMoO_4$–CoV_2O_6–CoO SYSTEM
Quasi-binary line $Co_3V_2O_8$–$CoMoO_4$

M. Kurzawa and M. Bosacka

Department of Inorganic Chemistry, Technical University of Szczecin, Al. Piastow 42
71–065 Szczecin, Poland

Abstract

The phase relationship in the pseudobinary $Co_3V_2O_8$–$CoMoO_4$ system have been determined by differential thermal analysis (DTA) and X-ray diffraction (XRD). A new compound $Co_{2.5}VMoO_8$, stable up to $1080\pm5^\circ C$ has been found in the system. The results obtained are presented in the form of a phase diagram.

Keywords: cobalt(II) orthovanadate–cobalt(II) molybdate system, cobalt(II) vanadium(V) molybdenum(VI) oxide, DTA, phase diagram, XRD

Introduction

In practical applications, mixed vanadium oxides and molybdenum oxides used in catalysts have been recommended in many heterogeneous oxidation processes [1–3]. To understand many of the reactions, basic informations on phase equilibria are necessary. Phase relations in the system $Co_3V_2O_8$–$CoMoO_4$ have not been established. The aim of the present work was to determine a comprehensive phase diagram of the system under consideration.

Cobalt(II) orthovanadate and cobalt(II) molybdate, the components of the title system, are well known. $Co_3V_2O_8$ is one of the three for-long known vanadates, that occur in the two-component system CoO–V_2O_5 [4, 5]. Cobalt(II) orthovanadate crystallizes in an orthorhombic system, space group Cmca, with 4 molecules in its unit cell having the following parameters: $a=6.030(4)$ Å, $b=11.486(2)$ Å, $c=8.312(5)$ Å [6]. $Co_3V_2O_8$ is isotypical with $Mg_3V_2O_8$, $Ni_3V_2O_8$ and a low-temperature modification of $Zn_3V_2O_8$ [6–8]. The compound melts incongruently at $1216\pm10^\circ C$, depositing CoO crystals [9].

The other component of the system, $CoMoO_4$, forms under atmospheric pressure two polymorphic modifications: a low-temperature α-$CoMoO_4$ and a high-temperature β-$CoMoO_4$ [10–12]. Transformations of the α-form into the β-form is fast and takes place at ~$400^\circ C$ [12]. The reverse transformation is hindered and takes place at much lower temperatures, depending on the conditions of the experiment [11]. Consequently, the β-modification can exist at room temperature as a metastable phase, and only when ground does it undergo a transformation into the low-temperature

form α-$CoMoO_4$ [10, 12]. The low-temperature modification crystallizes in a monoclinic system, space group C2/m, Z=8, a=9.666 Å, b=8.854 Å, c=7.755 Å, β=113°49' [13].

Likewise $MgMoO_4$, $ZnMoO_4$ and a high-temperature $NiMoO_4$ modification, β-$CoMoO_4$ is isostructural with α-$MnMoO_4$ [10], it crystallizes in a monoclinic system, space group C2/m. Parameters of its unit cell are: a=10.21 Å, b=9.31 Å, c=7.01 Å, β=106.4° [10]. There is also known a high-pressure modification of cobalt(II) molybdate of a $NiWO_4$ structural type [10]. This molybdate crystallizes in a monoclinic system, belongs to space group P2/c and parameters of its unit cell are: a=4.657 Å, b=5.682 Å, c=4.917 Å, β=90°45'. The high-pressure modification undergoes irreversible transition into a stable form at 660°C under atmospheric pressure [10]. According to the data published, the molybdate melts congruently at 1180°C [14].

Experimental procedure

The following reagents were used in the experiments: V_2O_5, MoO_3 and $CoCO_3$ (commercial products analytically pure, of POCh production, Gliwice, Poland). For the studies also used $Co_3V_2O_8$ and $CoMoO_4$ were prepared by calcination of the suitable reagents. Thus $Co_3V_2O_8$ was produced by heating a mixture of $CoCO_3$ with V_2O_5 at a molar ratio 3:1 at 600°C for 24 h, then at 750°C for 24 h and finally at 800°C for 96 h. $CoMoO_4$, in turn, was obtained by heating an equimolar mixture of $CoCO_3$ with MoO_3 at 600°C for 48 h and then at 650°C for 72 h. The diffraction patterns of both compounds indicated the absence of spurious phases.

For the measurements two series of samples were prepared: a basic series consisting of 14 samples made of suitable mixtures of V_2O_5, MoO_3 and $CoCO_3$ and verifying one of 3 samples made of phases building the system under study, that is, $Co_3V_2O_8$ and $CoMoO_4$. The parent substances were weighed in the given amounts, then homogenized by grinding and shaped into pastilles. The pastilles were placed in porcelain crucibles and heated in ambient air under conditions ensuring the set in of equilibrium, therefore all the samples were heated at 650°C for 72 h, 700°C for 24 h, 750°C for 24 h, 800°C for 24 h, 850°C for 24 h, 900°C for 24 h, 950°C for 24 h and 1000°C for 24 h. Information about the state of equilibrium was obtained by XRD, which was used for monitoring the composition of the samples after each of the heating cycles. Equilibria were assumed to be established when there were no further changes in the X-ray diffraction patterns.

Afterwards, all the samples after the final heating cycle still placed in the furnace were cooled slowly for about 12 h to ambient temperature. Next, the pellets were ground and examined by DTA and XRD methods.

In order to ascertain that the types of solid phases occurring in the subsolidus area of the system under study were correct, several selected samples of the basic series a new shaped into pastilles were extra heated for 24 h at 970°C. The samples were then quenched to ambient temperature, ground and examined by XRD method to determine their composition. In this way, all the kinds of arising phases and the ranges of their co-existence in the solid state have been established.

Phases occurring in the samples were identified by XRD method using a diffrac-
tometer DRON-3 with CoK_α radiation, Fe filter, and based on the data compiled in
the JP PDF cards [16] and the work [15].

DTA examinations made using a Derivatograph Q-1500 type of the MOM, Buda-
pest. All the measurements were carried out in a static air atmosphere, at 20–1500°C
and a constant heating rate of 10°C min^{-1}. The mass of each sample was 300 mg.
The measurements were made in alumina crucibles and Al_2O_3 powder as a reference.

Results and discussion

Table 1 shows compositions of initial mixtures and the results of XRD analysis
of samples obtained after the final stage of heating the mixtures of oxides with
$CoCO_3$ and mixtures of $Co_3V_2O_8$ with $CoMoO_4$. Data in Table 1 show that compo-
nents of the system fail to coexist in equilibrium. Samples obtained from mixtures of
oxides with $CoCO_3$, which contained up to 66.67 mol% of $CoMoO_4$ (in terms of
components of the system) in their initial mixtures turned out to be a mixture of two
phases: $Co_3V_2O_8$ and $Co_{2.5}VMoO_8$. A sample composed of 66.67 mol% of $CoMoO_4$
and 33.33 mol% of $Co_3V_2O_8$ after processing gave a preparation that consisted of
$Co_{2.5}VMoO_8$ only. Other preparations contained phases identified as $CoMoO_4$ and
$Co_{2.5}VMoO_8$. Accordingly, the composition of all the samples in the state of equilib-
rium – that is, those derived from oxides and those obtained from mixtures of
$Co_3V_2O_8$ with $CoMoO_4$ – indicates that the following reaction takes place in the
solid state:

$$Co_3V_2O_{8(s)} + 2CoMoO_{4(s)} = 2Co_{2.5}VMoO_{8(s)} \qquad (1)$$
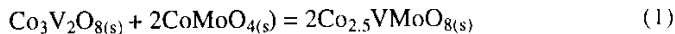
to yield $Co_{2.5}VMoO_8$, a compound the occurrence of which in the CoO–V_2O_5–MoO_3
system was confirmed recently [15]. It is within the component concentration range
of up to 66.67 mol% of $CoMoO_4$ that cobalt(II) molybdate reacts with $Co_3V_2O_8$ to
completion. At this concentration range, $Co_3V_2O_8$ remains in equilibrium with the
reaction product, that is, with $Co_{2.5}VMoO_8$. At the molar ratio of 2:1 for $CoMoO_4$ to
$Co_3V_2O_8$, the compounds interact stoichiometrically (Eq. 1). The extent of the reac-
tion can be confirmed by the composition of the sample obtained by heating a suit-

Table 1 Composition of initial mixtures and results from XRD analysis for all samples

Composition of samples/ mol% $CoMoO_4$	Reagents	Phases found
6.0; 10.0; 20.0; 30.0; 40.0; 50.0; 55.0; 60.0	V_2O_5, MoO_3, $CoCO_3$	$Co_3V_2O_8$, $Co_{2.5}VMoO_8$
40.0	$Co_3V_2O_8$, $CoMoO_4$	$Co_3V_2O_8$, $Co_{2.5}VMoO_8$
66.67	V_2O_5, MoO_3, $CoCO_3$	$Co_{2.5}VMoO_8$
66.67	$Co_3V_2O_8$, $CoMoO_4$	$Co_{2.5}VMoO_8$
70.0; 75.0; 80.0; 90.0; 94.0	V_2O_5, MoO_3, $CoCO_3$	$Co_{2.5}VMoO_8$, $CoMoO_4$
75.0	$Co_3V_2O_8$, $CoMoO_4$	$Co_{2.5}VMoO_8$, $CoMoO_4$

able mixture of $CoMoO_4$ with $Co_3V_2O_8$ (Table 1). Following Eq. (1), within the odd range of component concentrations, that is, beyond that with the 66.67 mol% of $CoMoO_4$ content in initial mixtures, the excessive reactant appears to be $CoMoO_4$. In addition, within this range, it is $CoMoO_4$ and $Co_{2.5}VMoO_8$ that remain in equilibrium in the subsolidus area.

Figure 1 shows a phase diagram of the $Co_3V_2O_8$–$CoMoO_4$ system, based on the DTA curves taken from samples of the basic and verifying series, and results from XRD examination of all samples. The temperatures of the solidus line were determined by onset temperatures of first endothermic effects recorded on DTA curves of the samples examined. The liquidus lines were delineated as well by reading onset temperatures of the effects observed as the last ones on DTA curves.
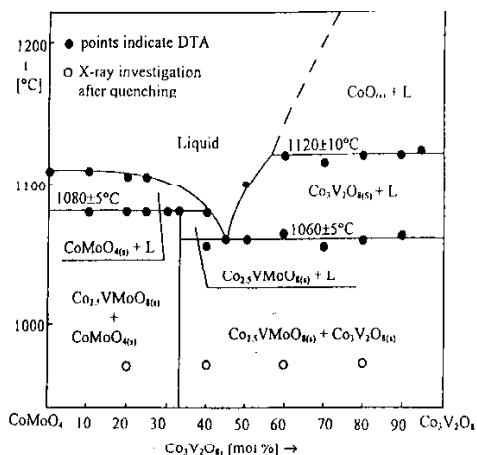

Fig. 1 Phase diagram of $Co_3V_2O_8$–$CoMoO_4$ system in an air atmosphere

The phase equilibrium diagram shown in Fig. 1 points out that only one compound, $Co_{2.5}VMoO_8$, occurs in the $Co_3V_2O_8$–$CoMoO_4$ system. The compound melted incongruently at 1080±5°C to deposit $CoMoO_4$ crystals, which was confirmed by XRD analysis of $Co_{2.5}VMoO_8$ additionally heated for 3 h at 1090°C and then quenched to ambient temperature. Cobalt(II) orthovanadate forms with $Co_{2.5}VMoO_8$ an eutectic (about 45.0 mol% of $Co_3V_2O_8$ and about 55.0 mol% of $CoMoO_4$) melting at 1060±5°C. Above the eutectic temperature, cobalt(II) orthovanadate and $Co_{2.5}VMoO_8$ remain in equilibrium with the melt. The subsolidus line within the crystalline zone of $Co_{2.5}VMoO_8$ is rather flat and the temperature window is quite narrow (Δt about 20°C). Over the component concentration range upwards to 66.67 mol% of $CoMoO_4$, $Co_{2.5}VMoO_8$ and cobalt(II) molybdate coexist in equilibrium up to the solidus line temperature, determined by the temperature of incongruent melting of $Co_{2.5}VMoO_8$, i.e. 1080±5°C. Above that temperature, the compound to be in equilibrium with liquid will be $CoMoO_4$. However, in some cir-

cumstances the experimental results were not ample and reliable enough to contribute to exact delimiting if the field that would enclose $CoO_{(s)}$+liquid in the high-temperature area of the phase diagram

Finally, it should be noted that $Co_{2.5}VMoO_8$ and $Co_3V_2O_8$ do not exhibit a phase transition up to their melting temperature when heated in air, thus $Co_{2.5}VMoO_8$ and $Co_3V_2O_8$ are stable in one modification. The DTA curve of $CoMoO_4$ shows a small endothermic effect with a peak onset temperature 400°C which corresponds to a polymorphic transition: $\alpha\text{-}CoMoO_4 \rightarrow \beta\text{-}CoMoO_4$.

Conclusions

The phase relationship in the $Co_3V_2O_8$–$CoMoO_4$ system were studied in air up to 1200°C using XRD and DTA methods. The following conclusions can be drawn from these studies:

• In solid state $Co_3V_2O_8$ and $CoMoO_4$ are not inert to one another but interreact to form a novel phase, $Co_{2.5}VMoO_8$.

• The compound $Co_{2.5}VMoO_8$ melts incongruently at 1080±5°C to deposit a solid $CoMoO_4$.

• Phase equilibria established in the $Co_3V_2O_8$–$CoMoO_4$ system within the whole concentration range of components up to 1200°C have been shown in the phase diagram (Fig. 1).

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