Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 973–976

THE PHASE DIAGRAM OF V_2O_5–MoO_3–Ag_2O SYSTEM
Part V. Phase diagram of the ternary system

E. Wenda[1*] *and A. Bielański*[1, 2]

[1]Faculty of Chemistry, Jagiellonian University, ul. R. Ingardena 3, 30-060 Cracow, Poland
[2]Polish Academy of Sciences, Institute of Catalysis and Surface Chemistry, ul. Niezapominajek 8, 30-239 Cracow, Poland

The paper summarizes the results concerning the different parts of the ternary system V_2O_5–MoO_3–Ag_2O and presents projection of the diagram on the basal triangle as well as its three-dimensional presentation of the diagram drawn by the AutoCAD programme.

Keywords: *molybdena, phase diagram, silver oxide, vanadia*

Introduction

The present publication summarises and gives final discussion of the previous papers by the present author concerning the particular sections of ternary diagram V_2O_5–MoO_3–Ag_2O [1–4]. The choice of this system as the object of investigations is relevant to the fact that vanadium-molybdenum catalysts are frequently used for the oxidation of hydrocarbons and especially of the aromatic ones [5, 6]. They contain additives of other oxides (e.g. P_2O_5, Ag_2O, Li_2O, NiO, etc.) as promoters. It has been shown that small amounts of silver oxide forming solid solution in the V_2O_5 structure are improving distinctly the selectivity in the benzene oxidation to maleic anhydride [7]. However at 9 or 12 mol% Ag_2O vanadium-molybdenum bronze was the only phase which was only weakly active catalytically. These facts indicate that the effect of the doping vanadium-molybdenum catalysts with silver oxide depends on the structure of the phase into which Ag_2O is introduced and necessitates the examination of the phase composition of silver oxide containing vanadium–molybdenum system i.e. the study of ternary diagram V_2O_5–MoO_3–Ag_2O. Independently of the above reasons this diagram is interesting also from the point of view of inorganic chemistry and never has been investigated by the earlier authors. The more that the number of investigated ternary systems containing vanadium and molybdenum oxides is limited [8–10].

Experimental

The present investigation of the ternary system comprised several stages. In the first one the binary systems: V_2O_5–MoO_3, V_2O_5–Ag_2O and MoO_3–Ag_2O were studied. In the V_2O_5–MoO_3 system [11] three phases appear: the solid solution of MoO_3 in V_2O_5, the intermediate compound $V_9Mo_6O_{40}$ and MoO_3 phase. In the V_2O_5–Ag_2O system [1] the number of detected phases is much larger. They are: solid solution of Ag_2O in V_2O_5, β-bronze $Ag_XV_{2-x}O_{5-x}$ and three incongruently melting compounds: $Ag_2V_4O_{11}$, β-$AgVO_3$ and Ag_3VO_4 (two latter ones are forming double eutectic), as well as Ag_2O/Ag. In the MoO_3–Ag_2O system [2] MoO_3 phase is forming double eutectic with the compound $Ag_2Mo_4O_{13}$ (20 mol% Ag_2O). The latter at higher Ag_2O content is forming an eutectic with the compound $Ag_2Mo_2O_7$ (33 mol% Ag_2O). Both latter compounds are fusing congruently. On the other hand the third compound of molybdenum and silver appearing in this system, β-Ag_2MoO_4 (50 mol% Ag_2O), is melting incongruently. The investigation of this system was strongly complicated by the sublimation of MoO_3 below its melting temperature and decomposition of Ag_2O at relatively low temperature (440°C). These two circumstances necessitated sintering the samples with high content of both latter oxides at possibly low temperatures not exceeding 400°C and this is why equilibration of the samples needed very long periods of time.

The following stage of the V_2O_5–MoO_3–Ag_2O system study was the investigation of the chosen sections of the ternary system. In particular the series of the samples were investigated in which at constant V_2O_5/MoO_3 molar ratio (9:1, 7:3, 1:1 and 3:7) the

* Author for correspondence: wenda@chemia.uj.edu.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

content of Ag_2O was changing from 1 to 90 mol% [3, 4]. A section of the ternary system was also investigated at which the content of Ag_2O was constant (50 mol% Ag_2O) at the changing V_2O_5/MoO_3 molar ratio, as well as binary systems including the triple phase $AgVMoO_6$.

Most of the samples investigated in the above mentioned publications [1–4] have been obtained by sintering the appropriate mixtures of V_2O_5, MoO_3 and Ag_2O in the atmosphere of air at temperatures below their melting points. Some samples (mainly those of the MoO_3–Ag_2O system) were obtained by melting oxide mixtures because phase equilibrium could not be reached by sintering. The choice of the sintering temperature was preceded by DTA analysis of the samples and sintering of oxide mixtures was carried out at temperature 30–50°C below that of the first endothermic peak which was assumed to correspond to the beginning of sample melting. Phase composition was established by XRD analysis. All details concerning the preparation of the samples, DTA and XRD analyses are given in papers [1–4, 11].

Results and discussion

The V_2O_5–MoO_3–Ag_2O phase diagram has been constructed on the basis of the results obtained in [1–4, 11] papers by the same author. Figure 1 shows the projection of the crystallization surfaces on Gibbs triangle. A three-dimensional presentation of the surface constructed by the use of Auto-Cad computer program is shown in Fig. 2.

The corners of Gibbs triangle correspond to 100 mol% V_2O_5, 100 mol% MoO_3 and 100 mol% Ag_2O. Silver oxide, not metallic silver, is taken as component because the thermal analysis of the oxide mixtures has shown that it is Ag_2O which reacts with the other oxides. Metallic silver appeared in the system in the case when the silver rich compounds: Ag_3VO_4 (above 75 mol% Ag_2O) and β-Ag_2MoO_4 (above 50 mol% Ag_2O) were present which are incongruently melting (450 and 575°C, respectively) with the segregation of metallic silver [1, 2]. At the conditions of high silver content our system should be treated rather as a quadruple system V_2O_5–MoO_3–Ag–O_2. No investigations were undertaken by us in this direction and, hence, the part of the diagram shown in Figs 1 and 2 corresponding to Ag_2O content higher than about 75–65 mol% remains empty.

All phases appearing in the binary systems are also present in the ternary system. The ternary phase $AgVMoO_6$ – isostructural with $NaVMoO_6$ – has not its analogue in binary systems. It has been described for the first time by the present authors [3].

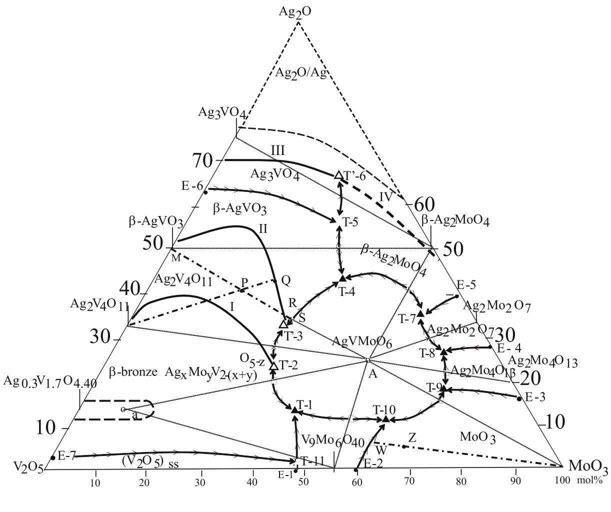

Fig. 1 The projection of V_2O_5–MoO_3–Ag_2O phase diagram on Gibbs triangle. •E – binary eutectic, ▲T – ternary eutectic, ΔT' – 'pseudo-ternary' eutectic points, A – maximal temperature point (625°C) on the crystallization field of $AgVMoO_6$, a – maximal temperature point (724°C) on the crystallization field of bronze corresponding to $Ag_{0.30}Mo_{0.08}V^{5+}_{1.54}V^{4+}_{0.08}O_{4.25}$ composition, > > > eutectic line, —— meritectic line, x – maximal temperature point on the eutectic line, ····· lines connecting compositions of two neighbouring compounds which create double eutectics

The following rules have been accepted in the presentation of the ternary diagram:

- The ternary eutectic points in the ternary system (zero degrees of freedom) are denoted as ▲T, 'pseudo-ternary' points (points on the cross section of eutectic and meritectic lines) are denoted as ΔT' and double eutectic points in the binary systems as •E.

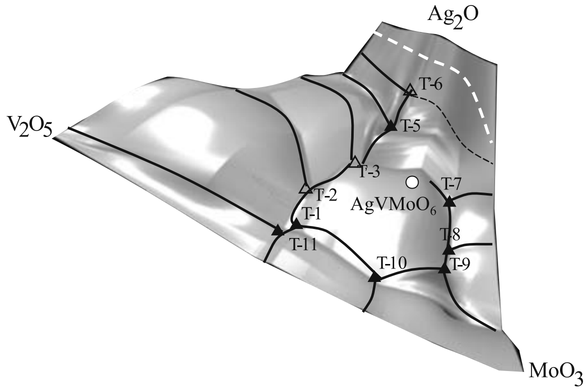

Fig. 2 Three dimensional presentation of V_2O_5–MoO_3–Ag_2O diagram drawn by the AutoCAD programme. The full lines show boundary curves, the triangles show ternary and 'pseudo-ternary' eutectics

- The lines of double eutectics in the ternary system are represented by the lines decorated with arrows showing the direction along which melting temperature of the double eutectic mixture decreases. If eutectic line joins points E and T in accordance with Alkemade rule [12, 13] temperature decreases monotonically along the line from E to T. A maximum of temperature appears on the line joining two points T–T denoted by x. Point x is situated at the cross section of the eutectic line with the line connecting the compositions of the compounds which crystallise along this eutectic line.
- The lines along which meritectic reactions take place are denoted by solid lines. They correspond to the following meritectic melting reactions:

I $Ag_2V_4O_{11}$↔β-bronze $Ag_xMo_yV_{2-(x+y)}O_{5-z}$+melt

II β-$AgVO_3$↔$Ag_2V_4O_{11}$+melt

III Ag_2O/Ag↔Ag_3VO_4+melt

IV Ag_2O/Ag↔β-Ag_2MoO_4+melt

Points ΔT'-2, ΔT'-3 and ΔT'-6 are pseudo-triple points. They correspond to the final stage of meritectic reactions I–IV.

The eutectic and meritectic lines determine the crystallisation fields of the particular phases appearing in the ternary system V_2O_5–MoO_3–Ag_2O. For example crystallisation field of the solid solution of MoO_3 in V_2O_5 is determined by points E-1, T-11, E-7 and V_2O_5 and the lines joining them. Crystallisation field of β-bronze is determined by points E-7, T-11, T-1, T'-2, point corresponding to the composition of $Ag_2V_4O_{11}$ and the lines joining them. On this field a maximum is present determined by point 'a' to which temperature 724°C and composition $Ag_{0.30}Mo_{0.08}V^{5+}_{1.54}V^{4+}_{0.08}O_{4.25}$ correspond.

It is characteristic for the compounds incongruently melting that the points representing their composition are not situated on their own fields of the crystallisation. The point representing composition of $Ag_2V_4O_{11}$ is situated on the crystallisation field of β-bronze. Similarly the point representing the composition of β-$AgVO_3$ is situated on the crystallisation field of $Ag_2V_4O_{11}$, point representing Ag_3VO_4 and β-Ag_2MoO_4 on the field of Ag_2O/Ag.

Crystallization in a ternary system is in most cases a fairly complicated process. It is illustrated by the two following examples: crystallization of the melt of composition given by point P (Fig. 1) and that of the melt of composition given by point Z. Point P (42 mol% V_2O_5, 18 mol% MoO_3, 40 mol% Ag_2O) is situated on the crystallization field of $Ag_2V_4O_{11}$ but the point corresponding to the composition of the latter compound lies on the crystallisation field of β-bronze. On cooling a melt of the composition given by point P segregates at first as $Ag_2V_4O_{11}$ and the composition of the melt is changing along the line P–Q. At point Q meritectic reaction (II) begins: $Ag_2V_4O_{11}$ dissolves, incongruent compound β-$AgVO_3$ crystallizes and the composition of the melt changes along the line Q–R. At R (point R is situated at the cross section of the line determined by point M representing composition of β-$AgVO_3$ and point P with line II) all $Ag_2V_4O_{11}$ is used. At this stage the only process is the crystallisation of β-$AgVO_3$ and the composition of the melt changes along the line R–S. At S segregation of double eutectic β-$AgVO_3$–$AgVMoO_6$ begins along the lines S–T'-3. At T'-3 the rest of the melt solidifies isothermally forming triple eutectic containing β-$AgVO_3$, $AgVMoO_6$ and once more $Ag_2V_4O_{11}$. The presented course of crystallization is confirmed by the data given in Table 2 [3], which present the phase composition of the equilibrated product and DTA analysis in Fig. 3 [3].

Similar processes of the resorption recurrence accompany reactions I, III and IV in the case of which final crystallisations take place in point T'-2 or T'-6.

Point Z (28.2 mol% V_2O_5, 65.8 mol% MoO_3 and 6 mol% Ag_2O) is situated on the crystallization field of congruently melting MoO_3. The latter is the primary product of crystallization of the melt. On cooling the sample the composition of the melt changes along the line Z–W. It is getting enriched in vanadium. At point W segregation of binary eutectic $V_9Mo_6O_{40}$–MoO_3 along the line W–▲T-10 begins. The rest of the melt solidifies isothermally at ▲T-10 giving ternary eutectic $V_9Mo_6O_{40}$–MoO_3–$AgVMoO_6$.

As already said Fig. 2 presents schematically three-dimensional visualisation of V_2O_5–MoO_3–Ag_2O phase diagram obtained with the aid of computer program Auto-CAD. Continuous lines additionally drawn are showing the boundary curves separating particular crystallisation fields.

Conclusions

The Gibbs diagram of ternary V_2O_5–MoO_3–Ag_2O system at Ag_2O concentration below 65–75 mol% has been given as the final result of a series of previous publications.

References

1 E. Wenda, J. Thermal Anal., 30 (1985) 879.
2 E. Wenda, J. Thermal Anal., 36 (1990) 1417.
3 E. Wenda and A. Bielański, J. Therm. Anal. Cal., 92 (2008) 921.
4 E. Wenda and A. Bielański, J. Therm. Anal. Cal., 92 (2008) 931.

5 C. L. Thomas, Catalytic Processes and Proven Catalysts, Academic Press, New York and London 1970.
6 A. Bielański and J. Haber, 'Oxygen in Catalysis', Marcel Dekker, New York 1991, p. 137.
7 A. Inglot and E. Wenda, Bull. Pol. Ac. Sci. Chem., 28 (1980) 815.
8 M. Kurzawa, Termochim. Acta, 189 (1991) 129.
9 K. Mocała, J. Ziółkowski and R. Dziembaj, J. Solid State Chem., 56 (1985) 84.
10 M. Kurzawa and M. Bosacka, J. Therm. Anal. Cal., 65 (2001) 451.
11 A. Bielański, K. Dyrek, J. Poźniczek and E. Wenda, Bull. Pol. Ac. Sci. Chem., 19 (1971) 507.
12 A. C. van Rijan van Alkemade, Z. Phys. Chem., 11 (1893) 289.
13 D. V. Malakhov, Calphad, 28 (2004) 209.

Received: January 15, 2007
Accepted: November 6, 2007

DOI: 10.1007/s10973-007-8341-z