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PHASE EQUILIBRIA IN THE SYSTEM $V_9Mo_6O_{40}$–$AlVMoO_7$

M. Kurzawa and G. Dąbrowska

Department of Inorganic Chemistry, Technical University of Szczecin, Al. Piastów 42
70-065 Szczecin, Poland

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Abstract

DTA and XRD methods were applied in studies on phase equilibria established in the system $V_9Mo_6O_{40}$–$AlVMoO_7$ up to 1000°C over the whole component concentration range. The results were presented in the form of a phase diagram.

Keywords: $AlVMoO_7$, phase diagram, $V_9Mo_6O_{40}$

Introduction

$V_9Mo_6O_{40}$ and V_2O_5–MoO_3 system, in which the compound exists, are an attractive subject of studies, mainly due to the industrially important catalytic properties of the oxides, V_2O_5 and MoO_3, and of the phases formed in the system of interest [1–4]. Mixtures composed of V_2O_5 and MoO_3 are effective catalysts of many reactions, for example oxidation of benzene to maleic anhydride, selective reduction of NO_x, and isomerization and hydrogenation of alkenes [5–7]. The mixtures $V_9Mo_6O_{40}$/solid solutions of MoO_3 in V_2O_5 [8], that is, the phases occurring in the system V_2O_5–MoO_3 are also used as catalysts for the selective oxidation of benzene [9]. It is known that addition of other oxides, such as Al_2O_3, can affect the activity, selectivity and stability of a catalyst. Quite often, a carrier for oxide contact catalysts V_2O_5/MoO_3, is Al_2O_3. It is also known that a mixture of solid Al_2O_3, V_2O_5 and MoO_3 forms a compound, $AlVMoO_7$ [10, 11]. This compound can also be prepared by a reaction taking place in the solid state between MoO_3 and $AlVO_4$ – a compound existing in the Al_2O_3–V_2O_5 system [10, 11].

In order to elucidate the catalytic process occurring on the surface of contact catalysts it is necessary to get reliable and comprehensive information. Such information can be acquired from the phase equilibrium diagram describing any given catalyst. Thus it seemed important to find how $V_9Mo_6O_{40}$ and $AlVMoO_7$ – the compounds present in the systems of catalytic oxides – would behave towards each other over the whole range of component concentrations and temperatures up to 1000°C.

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Structurally, the $V_9Mo_6O_{40}$ phase belongs to a homologous series M_nO_{3n-1} (M=V and/or Mo), M_3O_8 being obtainable when n=3 [12–15]. In this general formula, the molar proportions of vanadium and molybdenum change from $(V_{0.5}Mo_{0.5})_3O_8$ at 500°C to $(V_{0.6}Mo_{0.4})_3O_8$ at 600°C [12]. In the phase, 1/9 of the vanadium atoms are present as V^{4+} ions [8, 9, 12–15]. The $V_9Mo_6O_{40}$ crystallizes in monoclinic system of the spatial group C2, the parameters of its unit cell being: a=1.93611(7) nm, b=0.36250(1) nm, c=0.41215(2) nm, β=90.617(3)° [15]. $V_9Mo_6O_{40}$ melts congruently: according to Bielański [9] – at 635°C, Munch and Pierron [8] – at 650°C, and Jarman [13] found it melting at 677°C. We have stated that the melting temperature of $V_9Mo_6O_{40}$ is 640°C.

$AlVMoO_7$ crystallizes in the orthorhombic system, the parameters of its unit cell are as follows: a=0.53812(1) nm, b=0.81788(1) nm, c=1.27488(2) nm [11]. The compound melts incongruently at 690±10°C, depositing two phases: $Al_2(MoO_4)_3$ and Al_2O_3 [10, 11, 16].

Experimental

The following oxides were employed in the experiments: V_2O_5 and amorphous Al_2O_3 – analytically pure commercial products of POCh (Gliwice, Poland) and MoO_3 obtained by thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at 150–450°C in air. $V_9Mo_6O_{40}$ and $AlVMoO_7$ were also used in the studies. The $V_9Mo_6O_{40}$ phase was prepared by the co-precipitation method described by Jarman [12], consisting in the precipitation of the phase precursor by mixing suitable amounts of saturated solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and NH_4VO_3, gentle evaporation of the liquid, drying of the precipitate at 110°C to constant weight and then calcination at 600°C in three 6-hour cycles. $AlVMoO_7$, in turn, was obtained by heating an $Al_2O_3/V_2O_5/MoO_3$ mixture at a molar ratio of 1:1:2 for 72 h at 550°C and then for 48 h at 600°C. Diffraction patterns of the so obtained $V_9Mo_6O_{40}$ and $AlVMoO_7$ were consistent with the data contained in the P.D.F. charts [17] and with those given in [8, 11, 13].

Two series of samples were prepared: a basic series consisting of 18 samples composed of oxides and a verifying one (5 samples) including phases building the system under study, that is, $V_9Mo_6O_{40}$ and $AlVMoO_7$.

The oxides were weighed in suitable proportions, carefully homogenized by grinding and then shaped into pastilles. The pastilles were placed in porcelain crucibles and heated in ambient air under conditions ensuring establishment of equilibrium, that is, at 550°C for 72 h, then at 570°C in two 48 h cycles and finally at 590°C for 48 h. The conditions were established via additional experiments made with three oxide samples, the initial mixtures of which contained 25.0; 50.0; and 75.0 mol% of $AlVMoO_7$, respectively. Information about the equilibrium state was acquired by verifying the contents of the samples by X-ray phase diffraction made after successive stages of heating. When identical results were obtained after at least two consecutive heating stages, the equilibrium state was considered to be established and the heating was terminated. The heating temperature was determined based on DTA results.

Afterwards, all the samples of the basic series after the final heating cycle still in the furnace were cooled slowly in about 12 h to ambient temperature. The samples (in the form of pellets) so prepared were triturated and examined by DTA and X-ray methods to determine their composition.

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 and five mixtures $V_9Mo_6O_{40}/AlVMoO_7$ containing respectively 15.0; 30.0; 50.0; 70.0 and 85.0 mol% of $AlVMoO_7$ were heated additionally for 24 h at 600°C, viz. at a temperature lower by around 15°C than the temperature of the solidus line. The samples were then quenched to ambient temperature, triturated and examined by XRD for the types of solid phases contained in the samples. In this way, the types of the solid phases occurring in the subsolidus area of the system of interest were determined. In turn, the types of solid phases being in equilibrium with liquid in the high-temperature field of the phase diagram were determined based on the XRD analysis made for some selected samples additionally heated for 2–3 h at chosen temperatures within the range 620–820°C and then quenched to ambient temperature.

The phases occurring in the samples were identified based on the results of XRD analysis (X-ray diffractometer DRON-3, radiation CoK_α, filter Fe) and on the data compiled in PDF charts [17] and the information available in publications [8, 11, 13].

DTA was made using a derivatograph of the Paulik-Paulik-Erdey type (MOM Budapest), in quartz crucibles, in air at 20–1000°C and a heating rate of 10°C min^{-1}. The weight of each sample was 1000 mg. The measurements were made in quartz crucibles.

Results and discussion

The Fig. 1 shows a diagram of phase equilibria being established in the system $V_9Mo_6O_{40}$–$AlVMoO_7$ over the whole component concentration range and within that of temperatures up to 850°C.

The diagram was constructed on the basis of DTA curves and the XRD results obtained for all the samples being in a state of equilibrium. The solidus line temperature was determined based on the onset temperature of the first effect noted in the DTA curves of the measured samples. The liquidus curves were determined by reading the peak temperatures of the effects noted in the DTA curves and considered as final. The solid/liquid coexistence ranges were established on the basis of DTA results obtained for the equilibrium samples. The types of the phases were, in turn, specified depending on the XRD results obtained for the

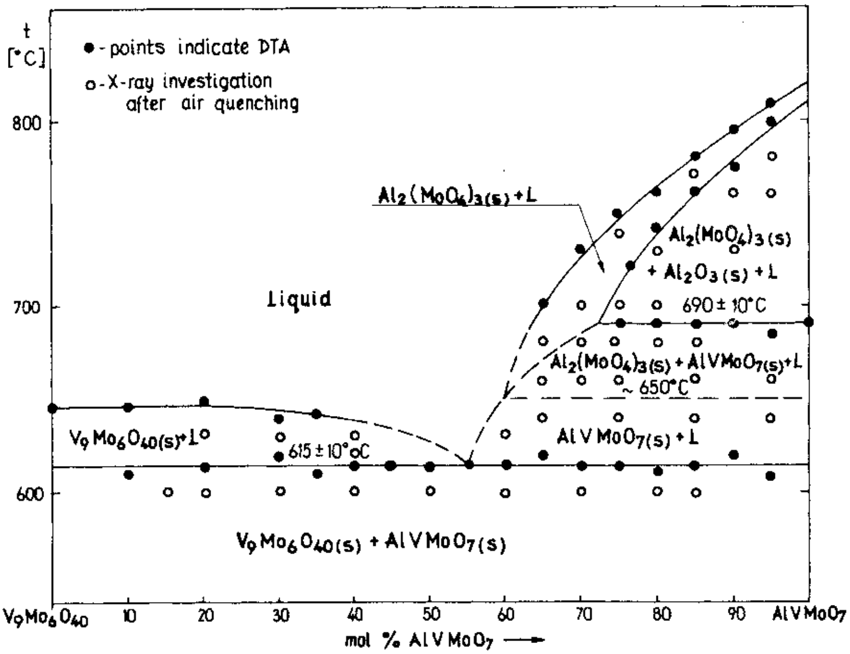

Fig. 1 Phase diagram of the $V_9Mo_6O_{40}$–$AlVMoO_7$ system

samples frozen at suitable temperatures. The compositions of the samples and the 'freezing' temperatures were marked in the Fig. 1.

It can be inferred from the phase diagram presented that the components of the system $V_9Mo_6O_{40}$–$AlVMoO_7$ remain in equilibrium up to the solidus line temperature. Whenever the title system contains 45 mol% of $V_9Mo_6O_{40}$ and 55 mol% of $AlVMoO_7$, there occurs an eutectic melting at 615±10°C. Above the eutectic temperature, the components are in equilibrium with a liquid. Above 650°C, in the appropriate phase diagram areas, the solid phases also remain in equilibrium with a liquid, the presence of which was not stated in the subsolidus area, that is, $Al_2(MoO_4)_3$ and Al_2O_3. The phases appear in the system due to the incongruent melting of $AlVMoO_7$.

$$AlVMoO_{7(s)} \rightarrow Al_2(MoO_4)_{3(s)} + Al_2O_{3(s)} + \text{liquid} \qquad (1)$$

However, in some circumstances, the experimental results were not sufficient in number and realiable enough to permit an exact delimitation of all the fields in which the solid phases would be in equilibrium with the liquid. Accordingly, the temperature range for the fields: $AlVMoO_{7(s)}$+liquid and $AlVMoO_{7(s)}$+$Al_2(MoO_4)_{3(s)}$+liquid have been established partially based on the XRD analysis of the samples heated in addition at temperatures higher than the solidus temperature, and then quenched to ambient temperature.

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