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PHASE RELATIONS IN THE SYSTEM $Al_2(MoO_4)_3$–V_2O_5

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Abstract

The phase equilibria established in the system $Al_2(MoO_4)_3$–V_2O_5 throughout the whole component concentration range up to 1000°C were investigated by DTA and XRD methods. The results are presented in the form of a phase diagram.

Keywords: aluminium molybdate, phase equilibria, vanadium(V) oxide

Introduction

In order to recognize the nature of processes occurring on catalysts, it is necessary to acquire information on the solids on the surface of which the catalytic action takes place. Such information is provided by phase equilibrium diagrams of the systems describing the given catalyst. Establishment of the phase equilibrium diagram of the system $Al_2(MoO_4)_3$–V_2O_5 is of interest, mainly because of the interesting catalytic properties of the components of the system [1, 2]. The phase relations in the system $Al_2(MoO_4)_3$–V_2O_5 throughout the whole component concentration range up to 1000°C have not yet been the object of comprehensive studies. Work on the reactivity of $Al_2(MoO_4)_3$ towards V_2O_5 in the solid state revealed only the phase equilibria established in the subsolidus area of the system under consideration [3].

Experimental

For the experiments the following reagents were used: V_2O_5, p.a. (POCh, Gliwice, Poland) and $Al_2(MoO_4)_3$, obtained by calcination of a mixture of amorphous Al_2O_3 and MoO_3 (in slight excess) at 700°C until constant mass was achieved, and then at 750°C for 24 h.

In order to obtain in-depth knowledge on the phase relations established in the title system, 18 samples composed of V_2O_5 and $Al_2(MoO_4)_3$ were prepared. The reagents, weighed in suitable proportions, were shaped into pastilles after homogenization and were then heated in ambient air under conditions ensuring the establishment of equilibrium. All the samples were heated at 550°C for 24 h and at 570°C over two 48 h cycles. The samples whose intitial mixtures contained over 64 mol% of V_2O_5 were additionally heated at 570°C for 72 h. Finally, all the samples were ground and

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examined by DTA and by XRD to determine their compositions. In this way, all the phases present and the ranges of their co-existence in the solid state were established.

The phases appearing in the samples were identified by means of XRD (a DRON-3 diffractometer, CoK_α radiation, and an Fe filter) and by comparing the results obtained with the data included in the JC PDF cards [4] and with those in [5].

The DTA measurements were made with a Paulik-Paulik-Erdey derivatograph, in air, in the temperature range 20–1000°C, at a heating rate of 10°C min^{-1}. Quartz crucibles were used in the experiments and the mass of each sample was 1000 mg.

Results and discussion

Table 1 lists the contents of the initial mixtures and the results of XRD analysis of all the samples at equilibrium. The data in Table 1 indicate that $Al_2(MoO_4)_3$ does not remain in equilibrium with V_2O_5 in the solid state. They also prove that, depending on the contents of their initial mixtures, $Al_2(MoO_4)_3$ and V_2O_5 interact to form a variety of solid phases which coexist in equilibrium in the solid state. The facts are consistent with the results of our earlier studies on the reactivity of $Al_2(MoO_4)_3$ towards V_2O_5.

Table 1 Contents of initial mixtures and XRD results on samples in an equilibrium state

Contents of V_2O_5 in inital mixtures/mol%	Phases identified
10.00; 20.00	$Al_2(MoO_4)_3$, $AlVMoO_7$, $V_9Mo_6O_{40}$ (traces)
30.00; 40.00; 50.00; 55.00; 60.00	$Al_2(MoO_4)_3$, $AlVMoO_7$, $V_9Mo_6O_{40}$
63.64	$AlVMoO_7$, $V_9Mo_6O_{40}$
67.00; 69.50; 73.00	$AlVMoO_7$, $V_9Mo_6O_{40}$, $V_2O_{5(s.s.)}$
76.96	$AlVMoO_7$, $V_2O_{5(s.s.)}$
80.00; 83.00; 86.00	$AlVMoO_7$, $AlVO_4$, $V_2O_{5(s.s.)}$
88.89; 92.00; 96.00	$AlVO_4$, $V_2O_{5(s.s.)}$

The phase equilibrium diagram established in the system $Al_2(MoO_4)_3$–V_2O_5 throughout the whole component concentration range to 1000°C is presented in Fig. 1. The phase diagram was constructed on the basis of the thermal effect temperatures recorded in the DTA curves and of the XRD results on all the samples obtained. Solidus line temperatures were determined by using the onset temperatures of the first endothermic effects, and liquidus lines by reading the onset temperatures of the endothermic effects, recorded as the last ones. The natures of solid phases in equilibrium with liquid were identified via the XRD results obtained on samples 'frozen' at appropriate temperatures. It follows from the diagram that the system $Al_2(MoO_4)_3$–V_2O_5 is not a real two-component system, even in the subsolidus area. This can be proved by the presence of fields in which three phases are in equilibrium, i.e. the following fields: $[Al_2(MoO_4)_{3(s)}+AlVMoO_{7(s)}+V_9Mo_6O_{40(s)}]$, $[AlVMoO_{7(s)}+V_9Mo_6O_{40(s)}+V_2O_{5(s.s.)}]$ and $[AlVMoO_{7(s)}+AlVO_{4(s)}+V_2O_{5(s.s.)}]$, and also the fields in which $AlVO_4$ is in equilibrium with a solid solution of MoO_3 in V_2O_5.

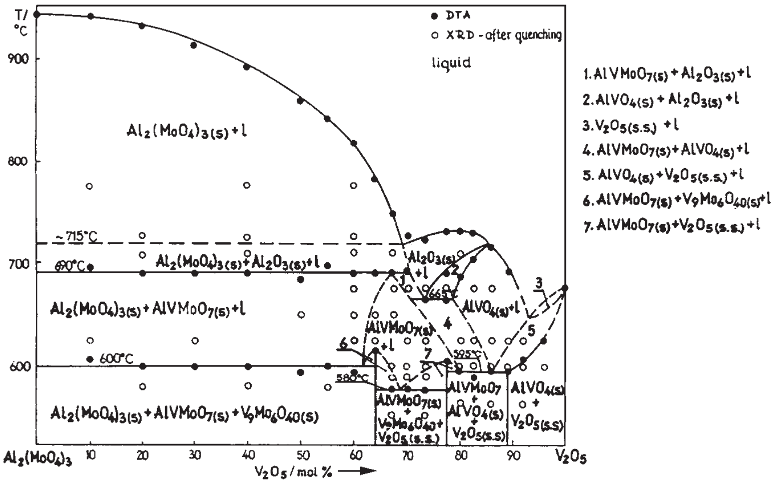

Fig. 1 Phase diagram of the system $Al_2(MoO_4)_3$–V_2O_5

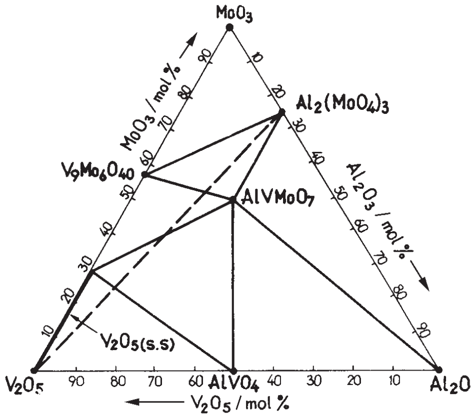

Fig. 2 Position of the section $Al_2(MoO_4)_3$–V_2O_5 in the three-component system Al_2O_3–V_2O_5–MoO_3

The phase relations in the system $Al_2(MoO_4)_3$–V_2O_5 imply that this system is only a section of the three-component system Al_2O_3–V_2O_5–MoO_3 (Fig. 2). The phase diagram of the system $Al_2(MoO_4)_3$–V_2O_5 also shows that the subsidiary systems are eutectics and yields information on the melting temperatures of tertiary eutectics. Accordingly, the tertiary eutectic $Al_2(MoO_4)_3$, $AlVMoO_7$, $V_9Mo_6O_{40}$ melts at 600°C, the eutectic $AlVMoO_7$, $V_9Mo_6O_{40}$, $V_2O_{5(s.s.)}$ at 580°C, and the eutectic $AlVMoO_7$, $AlVO_4$, $V_2O_{5(s.s.)}$ at 595°C.

Within the high-temperature area of the phase diagram, peritectic reactions are involved in the system, because of the incongruent melting of $AlVMoO_7$ and $AlVO_4$:

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

$$AlVO_{4(s)} \rightarrow Al_2O_{3(s)} + \text{liquid} \quad (2)$$

The experimental results did not always fix the limits of existence in the high-temperature area of the phase diagram, for the fields in which solid phases coexist in equilibrium with liquid, and the fields have therefore been marked with interrupted lines.

Summary

- The system $Al_2(MoO_4)_3$–V_2O_5 is not a real two-component system, even in the subsolidus area, and makes a section of the three-component system Al_2O_3–V_2O_5–MoO_3 (Fig. 2).
- The phase equilibria established throughout the whole component concentration range up to 1000°C have been illustrated by the phase diagram (Fig. 1).

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