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STUDIES ON THE SYSTEM Al_2O_3 - V_2O_5 - MoO_3

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Studies on the three-component system Al_2O_3-V_2O_5-MoO_3 have shown the existence of a new compound with molecular formula $AlVMoO_7$. The synthesis conditions and X-ray characteristics of this compound and its melting temperature, 690±10°C, are reported.

A knowledge of the phase equilibria in systems whose components or phases exhibit catalytic properties is of fundamental importance in the search for new catalysts with high selectivity and activity. The system Al_2O_3-V_2O_5-MoO_3 is such a system. A literature survey has shown that it has not yet been subject to investigation. In studies of systems of the type M_2O_3-V_2O_5-MoO_3 in which M = Fe [1-4] or Cr [5, 6], it was found that all three transition metal oxides participated in the formation of compounds. In studies on the system with M = Al, we have examined whether analogous compounds arise in the system Al_2O_3-V_2O_5-MoO_3.

The components of the system under consideration are well known [7-9], but the system V_2O_5-MoO_3 is undoubtedly the best known of the two-component systems [4, 10-12].

Experimental

Analar V_2O_5, pure MoO_3 and a commercial amorphous product, calcined pure Al_2O_3 (POCh, Poland), were used in the experiments. DTA was performed in air, in quartz crucibles at 20-1000°, and at a heating rate of 10 deg/min, using a Paulik-Paulik-Erdey derivatograph (MOM, Budapest). The weight of each sample was 1000 mg. The phase compositions of the preparation obtained were established by means of X-ray powder diffraction, using a diffractometer of type A_2 with an HZG-4 goniometer (CoK α),

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via the data included in the ASTM cards [13] and literature publications [14, 15].

Mixtures of the oxides were prepared the following reactions being assumed in the solid state:

$$Al_2O_{3(s)} + V_2O_{5(s)} + 2\,MoO_{3(s)} = 2\,AlVMoO_{7(s)} \quad (1)$$

$$2\,Al_2O_{3(s)} + V_2O_{5(s)} + 3\,MoO_{3(s)} = Al_4V_2Mo_3O_{20(s)} \quad (2)$$

After being ground down and pastilled, the mixtures of oxides with the molar ratios indicated in reactions 1 and 2 were calcined under the following conditions:

- the mixture with the composition corresponding to reaction 1: in three cycles at 600° for 48 h,
- the mixture with the composition corresponding to reaction 2: 600° (48 h x 2), 650° (48 h), 680° (48 h).

A mixture was also prepared with composition corresponding to the reaction

$$AlVO_{4(s)} + MoO_{3(s)} = AlVMoO_{7(s)} \quad (3)$$

This mixture was homogenized by grinding, pastilled and calcined at 600° (24 h x 2). After each calcination cycle, the preparations were slowly cooled down to ambient temperature, ground down, analyzed by DTA and X-ray powder diffraction, then again pastilled and calcined.

Results and discussion

For the preparation with an initial composition corresponding to reaction 1, as early as after the first calcination cycle the X-ray powder diffraction patterns revealed not only the sets of reflexions characteristic of the starting oxides, but also the presence of undefined reflexions that implied the formation of a new phase. After the third (the last) calcination cycle, only undefined reflexions were present in the diffraction pattern, with no initial oxides or other known phases. An identical set of diffraction lines was found in the diffraction pattern of the preparation obtained by reaction 3. Table 1 gives the interplanar distances for $AlVMoO_7$ and the relative intensities for the corresponding reflexions.

Table 1 Interplanar distances for $AlVMoO_7$ and relative intensities for the corresponding reflexions

d, Å	I, %
6.38	14
4.49	30
4.24	75
4.11	10
4.09	15
4.02	4
3.89	6
3.85	5
3.77	100
3.67	8
3.49	3
3.40	5
3.19	15
3.15	48
3.09	12
2.90	55
2.74	9
2.69	27
2.60	5
2.51	6
2.43	2
2.39	2
2.37	5
2.29	8
2.27	6
2.21	10
2.19	12
2.12	2

Figure 1 shows the DTA curve of $AlVMoO_7$. The first and largest endothermic effect, beginning at $690\pm10^{\circ}$, is attributed to the melting of $AlVMoO_7$. The mode of melting and other basic properties of this phase require further investigations.

The preparations whose initial compositions correspond to the substrates of reaction 2 (examined after each calcination cycle), contain $Al_2(MoO_4)_3$ and $AlVMoO_7$ or $Al_2(MoO_4)_3$ and V_2O_5, respectively, depending on the calcination temperature. This implies that, under the synthesis conditions, a phase with the molecular formula $Al_4V_2Mo_3O_{20}$ does not arise.

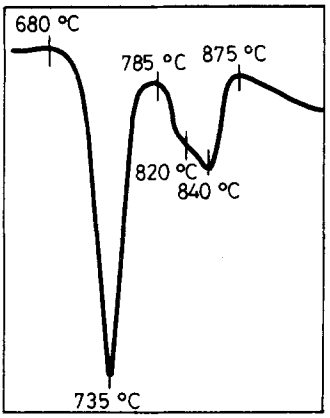

Fig. 1 DTA curve of $AlVMoO_7$

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Zusammenfassung — Einleitende Untersuchungen am Dreikomponentensystem Al_2O_3-V_2O_5-MoO_3 zeigten die Existenz einer neuen, noch nicht publizierten Verbindung der Formel $AlVMoO_7$. Die Synthese der Verbindung sowie ihre röntgenographischen Eigenschaften wurden beschrieben. Ihr Schmelzpunkt beträgt 690±10°C.