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Studies on the Vanadium Pentoxide — Molybdenum Trioxide System. II *. Phase Analysis

ARNE MAGNÉLI and BIRGITTA BLOMBERG

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

Rieck [1] has shown by means of thermal analysis that molybdenum trioxide and tungsten trioxide do not give solid solutions with each other. As these two metals have the same atomic radii the lack of extended homogeneity ranges of the trioxide phases must be connected with the different crystal structures of these substances **. It has recently been pointed out that there exists a remarkable relationship between the structures of vanadium pentoxide and molybdenum trioxide [3]. We thus found it of interest to examine the systems of vanadium pentoxide with molybdenum trioxide and also with tungsten trioxide. This paper will give an account of the results of a phase analysis performed for the former system.

Weighed mixtures of vanadium pentoxide and molybdenum trioxide (both of *puriss.* grade) were heated in evacuated silica tubes (for one day at about 700° C) or in porcelain crucibles (for one day at 600° C and several days at 650° C). No analysis was thought necessary for the former preparations. The latter, however, suffered a slight loss of weight during the heat treatment. The vanadium content of these preparations was determined by permanganate titration after reduction to the quadrivalent state by means of sulphur dioxide, which does not affect molybdic acid in a sulphuric acid solution [4]. Both vanadic and molybdic acids are reduced by cadmium (to V^{2+} and Mo^{3+}) and it was thus possible to find the combined content of vanadium and molybdenum by permanganate titration after percolating a sulphuric acid solution of the sample through a cadmium reducer [4,5].

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* I. *Acta Chem. Scand.* 5 (1951) 581.

** An intermediate phase of the approximate composition $MoWO_6$ has previously been shown to exist in the system molybdenum trioxide — tungsten trioxide [2]. An attempt to determine the crystal structure of this compound is in progress.

Table 1. Results of the phase analysis.

Composition of the preparation		Appearance of the preparation	Phases observed	Unit cell dimensions in Å (true Å units [7])			Density observed
Mol fraction of MoO_3 u	Fraction of V atoms substituted in the V_2O_5 phase x			a	b	c	
0	0	Brownish yellow powder	V_2O_5	11.505 ± ± 0.01	4.373 ± ± 0.003	3.564 ± ± 0.003	3.37
0.075	0.045	Greyish black crystal powder	V_2O_5				3.40
0.145	0.09	»	V_2O_5	11.55	4.33	3.575	3.46
0.215	0.14	»	V_2O_5	11.60	4.29	3.595	3.54
0.275		»	V_2O_5 + I	11.63	4.26	3.61	
0.36		»	I(+V_2O_5)				
0.44		»	I				
0.50		»	I				3.73
0.57		»	I				
0.70		Mixture of black and colourless crystals	I(+MoO_3)				
0.82		»	MoO_3 + I	3.95	13.85	3.69	
1		Almost colourless (slightly greenish) crystals	MoO_3	3.966	13.85	3.696[8]	

The phase analysis was performed by taking X-ray powder photographs of the various preparations in Guinier focusing cameras (with monochromatized Cu-$K\alpha$ radiation). The photographic film was covered by a thin aluminium

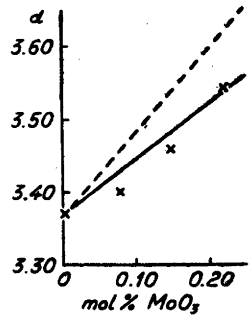

Fig. 1. Comparison between the observed densities (x) of solid solutions of molybdenum trioxide in the vanadium pentoxide phase and calculated densities corresponding to a) substitution of n *vanadium atoms by* 5n/6 *molybdenum atoms (full line) and b) substitution of vanadium atoms by the same number of molybdenum atoms and addition of oxygen atoms to the lattice in order to maintain electroneutrality (dashed line). (The latter alternative is very improbable from a crystallographic point of view.)*

foil (10 μ) in order to reduce the background due to the fluorescence of the vanadium. Powder photographs taken in high angle Phragmén-Hägg focusing cameras with Cr-K radiation were used for the precision determination of the lattice constants. The results of the phase analysis are summarized in Table 1. Three phases have been found to occur in this system at the aforementioned temperature.

The vanadium pentoxide phase shows a considerably extended homogeneity range. The lattice dimensions obtained for the pure substance are in close agreement with those recently reported by Byström, Wilhelmi, and Brotzen [6]. The variations of the unit cell dimensions show the homogeneity range of the phase to extend to a mol fraction of molybdenum trioxide, u, approximately equal to 0.25.

In order to elucidate the way in which molybdenum trioxide is taken up by the vanadium pentoxide lattice the densities of the various preparations were determined (Table 1). Fig. 1 shows the good agreement between the experimentally obtained values and those derived assuming that a number, n, of vanadium atoms are substituted by $5n/6$ molybdenum atoms. Electroneutrality is thus maintained by the appearance of vacant metal atom positions ($n/6$) accompanying the entrance of the molybdenum atoms. The mol fraction of 0.25 for the maximum solubility of molybdenum trioxide in the vanadium pentoxide phase evidently corresponds to about 17 per cent. of the vanadium atoms being substituted in this way. No extra lines which would indicate an ordered distribution of the molybdenum atoms could be observed in the powder photographs. The considerable solubility of molybdenum trioxide in the vanadium pentoxide phase is obviously dependent on the relationship between the crystal structures of these two oxides [3]. The changes of the coordination conditions accompanying the solubility process have also been previously discussed [3].

Powder photographs of the preparation with u equal to 0.36 showed traces of the vanadium pentoxide phase, together with the lines of an intermediate phase (I of Table 1). The latter appeared alone in photographs of preparations with u values around 0.5, but when u had reached 0.70 lines of molybdenum trioxide also became visible. The homogeneity range of the intermediate phase must thus be situated somewhere between the limits u equal to 0.36 and 0.70, and is probably rather narrow as no considerable variations in the positions of the reflections have been observed in the various photographs. The composition of the compound is likely to correspond to u equal to 0.5, *i. e.* to be V_2MoO_8.

The reflections of molybdenum trioxide occur at the same positions in the photographs of the pure substance and in those of specimens also containing the intermediate compound. The homogeneity range of the molybdenum trioxide phase in this system is evidently very narrow. This lack of solubility must imply that the molybdenum trioxide lattice offers a resistance to the introduction of extra atoms or the removal of oxygen atoms (the latter alternative being required by a hypothetical substitution of sexavalent molybdenum atoms by quinquevalent vanadium atoms). This stability of the molybdenum trioxide lattice appears very natural from the crystallochemical point of view.

It is interesting to note that all the intermediate preparations have a greyish-black colour in contrast to those of the pure oxides. This may be connected with the existence of a state of resonance between the vanadium and molybdenum atoms. Rough quantitative measurements of the electric conductivity of powder specimens of a few intermediate products carried out by Mr. Lars Kihlborg have given very low values.

SUMMARY

A phase analysis of the vanadium pentoxide — molybdenum trioxide system carried out on the basis of X-ray powder photographs of preparations obtained at 650°—700° C has revealed the existence of an intermediate phase having the probable composition V_2MoO_8.

The vanadium pentoxide phase shows an extended homogeneity range, the solid solutions being represented by the formula $V_{2(1-x)}Mo_{5x/3}O_5$ with the maximum value of x approximately equal to 0.17.

No signs indicating an extended homogeneity range of the molybdenum trioxide phase were observed.

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