JOURNAL OF SOLID STATE CHEMISTRY **26**, 339–343 (1978)

The Effect of the Gas Atmosphere on the Phase Transformation in the Solid Solution of MoO_3 in V_2O_5

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Received February 2, 1978; in revised form May 10, 1978

The nature of the structure transformation occurring under the influence of oxidizing or reducing gas atmosphere in powdered oxide $(V_2O_5)_{0.93}$ $(MoO_3)_{0.07}$ has been investigated. The formation of an intermediate compound in the inner parts of the catalyst grains during the oxidation and in the subsurface layers during the reduction has been observed.

Introduction

The V_2O_5–MoO_3 system has been extensively studied mostly in relation to the use of vanadium-molybdenum catalysts for aromatic hydrocarbon oxidation. Khulbe *et al.* (*1*) have observed the existence of a solid solution of V_2O_5 in MoO_3 in the preparations containing up to 2 mole% of V_2O_5. The existence of a solid solution of MoO_3 in V_2O_5 has been demonstrated in the samples containing no more than 30 mole% of MoO_3 (*2–5*). For higher concentrations of molybdenum, an intermediate compound (I.C.) has been found besides the V_2O_5 phase (*2–8*). From the investigation of Munch and Pieron (*6*) and also Bielański *et al.* (*4*) it may be concluded that the composition of the intermediate compound existing in equilibrium with the melt is $V_9Mo_6O_{40}$. On the other hand Magneli and Blomberg synthesized by a solid-state reaction the compound V_2MoO_8 (*2, 7, 8*).

The existing data concerning the solubility of MoO_3 in solid V_2O_5 show that at the eutectic temperature (about 610°C) 25–30% mole MoO_3 may enter into V_2O_5 lattice. With decreasing temperature solubility decreases, which as has recently been shown in (*9*) is accompanied by the segregation of $V_9Mo_6O_{40}$ phase. At 500°C and lower temperatures this solubility is between 10 and 15 mole% MoO_3.

Some experiments carried out in our laboratory using microprobe analysis have shown that certain segregation of vanadium and molybdenum in V_2O_5–MoO_3 solid solution may also take place in the course of reducing or oxidizing the samples. Such segregation is due to the different velocities of diffusion of vanadium and molybdenum: In the case of reduction the diffusion occurs from the surface layer to the bulk of crystallites; in the case of oxidation it occurs in the opposite direction.

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0022-4596/78/0264-0339$02.00/0

Printed in Great Britain

The aim of the present investigation was to state whether such dynamic segregation of both elements in the solid solution may also result in the formation of intermediate compound in the region enriched in molybdenum.

Experimental

A preparation containing 7 mole% MoO_3 and 93 mole% of V_2O_5 was used for investigation. It was obtained by fusing an appropriate mixture of analytically pure oxides, the X-ray analysis of which had shown only the presence of V_2O_5 resp. MoO_3 phase. The mixture was heated at 700°C for 2 hr and subsequently was slowly cooled (80°/hr). On cooling, the evolution of oxygen gas from the solidifying mass was observed. The powdered preparation was passed through a 60-μm mesh sieve. It contained about 5% of vanadium in the form of V^{4+} ions introduced in the course of the formation of solid solution according to the equation:

$$2MoO_3 \rightarrow 2Mo_V^{\cdot} + 5\,O_0 + 2e' + \tfrac{1}{2}O_{2(g)}.$$

Two series of experiments were carried out. The results are shown in the Fig. 2 (Results of series I are represented by circles, series II by squares.) In both cases the samples were at first oxidized by heating in the air at 450°C. Subsequently they were reduced by decomposing it *in vacuo* (10^{-6} Torr) at the same temperature. At various periods the treatments were interrupted, the sample cooled and tested roentgenographically, after which the treatment was again continued. In series II of experiments, after the period of oxidation and reduction, the sample was again oxidized in order to test the reversibility of the observed processes.

The X-ray phase analysis was performed using TUR-61 X-ray diffractograph with a copper lamp as a radiation source ($K\alpha =$ 1.538 Å). A 18-μm-thick nickel filter was used in order to eliminate $K\beta$ radiation. X-ray analysis of reduced samples was carried out immediately after the transfer of the sample from the vacuum cell to the X-ray equipment in order to avoid the oxidation of the sample by the air. The interval between the transfer of the sample from the vacuum system and the end of the X-ray measurements was not longer than 4 hr. In order to diminish the influence of the sample texture on the ratio of the intensities of reflections the preparations were sieved through the 60-μm mesh sieve before each measurement. The investigated sample was then shaped by a gentle pressing of the powder with a glass plate. As in the range of 8–14° in all difractograms the reflections (200) of the intermediate compound were present; this particular part of the X-ray pattern was chosen for monitoring the contents of I.C. When the I.C. concentration was relatively high other reflections of this phase were observed as well. The typical diffractograms obtained in the θ range of 8–14° for the sample with the highest contents of I.C. and for the sample with relatively small contents are presented in Fig. 1.

The I.C. reflections were observed also for the initial samples. The I.C. presence was due to incomplete homogenization in the course of preparing the samples. It was recently shown that this inhomogeneity disappeared if the sintered sample was annealed at the temperature above 350°C (*9*).

Table I gives the values of the interplanar distance for I.C. produced in various stages of redox processes. The observed deviations of the values of interplanar distances from those given by Munch *et al.* (*6*) and the dependence of these values on the content of I.C. are probably connected with some degree of disorder existing in the intermediate compound crystal lattice. As a measure of relative content of I.C. the ratio of intensities measured as the heights of the diffraction reflections (200) of I.C. and (201) of V_2O_5 was taken. The changes in I.C. content during oxidation and reduction are shown in Table II and in Fig. 2. In column 2 of Table II the details of the sample treatment before X-ray investigation are given. As can be seen from the Table II

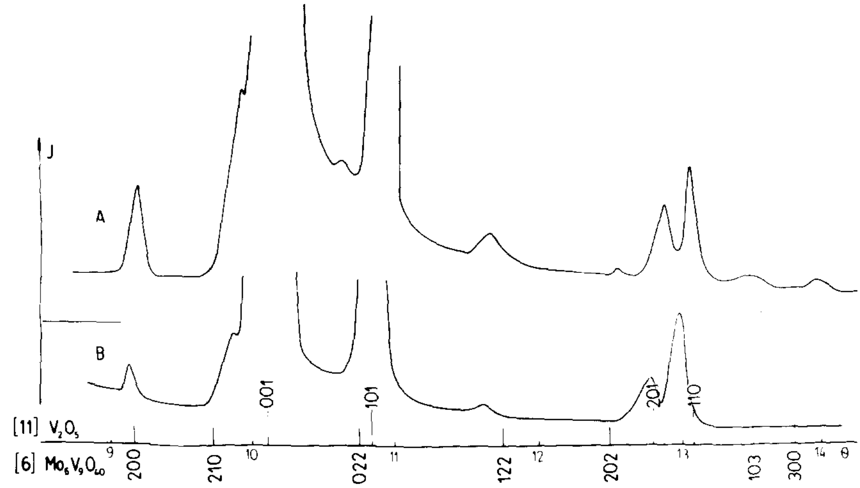

FIG. 1. X-ray diffraction patterns for: (A) the most reduced sample of the series I. (B) the sample of series I after the first stage of reduction.

and Fig. 2 the oxidation of the powdered samples of the catalyst results in the formation of the I.C. (points 2, 3, Fig. 2). The vacuum reduction of the same samples results initially in the partial disappearance of previously formed I.C. phase (point 4 and 5). After a 10-hr process of reducing the samples the content of I.C. is not very much higher than it was in the initial stage. A further reduction however is accompanied by a new increase in I.C. content (points 6 and 7). In series II of experiments the reversibility of the observed processes was also tested by oxidizing the reduced sample. Figure 2 shows that, in fact, during reoxydation the content of I.C. first decreases to a minimum (points 8, 9, 10) and then again increases (points 11, 12).

The observed results may be explained as follows. In the course of the oxidation period oxygen is incorporated into the external layer of V_2O_5 lattice. This must necessarily be accompanied by the diffusion of cations from the bulk to the surface. As it was shown in (*10*) the diffusion of vanadium atoms is faster than that of molybdenum atoms. This means that the surface layer becomes enriched in vanadium, and in lower layers of the crystallites the concentration of molybdenum does

TABLE I

THE INTERPLANAR DISTANCES OF $V_9Mo_6O_{40}$ OBSERVED AT VARIOUS STAGES OF REDOX TREATMENT OF THE SAMPLE IN SERIES I OF EXPERIMENTS

	d (Å)						
hkl	By Munch (*6*)	Exp. 1	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7
(200)	4.833	4.830	4.818	4.850	4.844	4.834	4.818
(210)	4.557	4.476	4.478	4.503	4.493	4.487	4.458
(022)	4.118	—	4.165	—	—	—	4.179
(122)	3.782	—	3.818	3.829	3.827	3.831	3.812
(202)	3.558	—	—	—	—	—	3.556
(103)	3.299	—	3.279	—	—	—	3.229
(300)	3.228	—	—	—	—	—	3.188

TABLE II

THE RELATIVE CONTENT OF THE INTERMEDIATE COMPOUND IN THE SAMPLES OF $(V_2O_5)_{0.93}(MoO_3)_{0.07}$ MIXED OXIDE IN THE COURSE OF OXIDIZING, REDUCING, AND REOXIDIZING TREATMENT

No. of experiment	Treatment of the sample	Series of experiments	$\frac{h_{200} \text{ of I.C.}}{h_{201} \text{ of } V_2O_5}$
1	Fresh powdered sample	I	0.35
		II	0.34
2	8.5 hr oxidation	II	0.95
3	24 hr oxidation	I	0.95
		II	0.97
4	2 hr reduction	I	0.73
5	10 hr reduction	I	0.52
		II	0.49
6	18 hr reduction	I	0.73
7	28 hr reduction	I	1.23
		II	1.28
8	2 hr reoxidation	II	0.79
9	5 hr reoxidation	II	0.40
10	10 hr reoxidation	II	0.21
11	18.5 hr reoxidation	II	0.51
12	28 hr reoxidation	II	0.55

increase. Our experiments indicate that locally the solubility limit of MoO_3 in V_2O_5 lattice is exceeded and the segregation of I.C. occurs.

During the reduction period, oxygen is removed from the external layers of the crystallites and this brings about inward diffusion of cations. Because the diffusion of vanadium is always faster this process at first

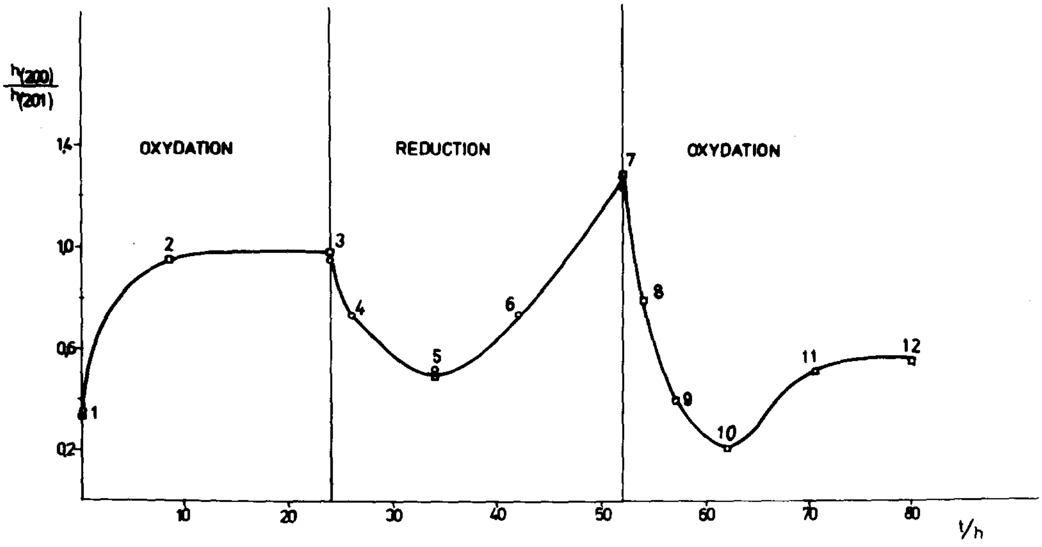

FIG. 2. The dependence of the relative content of intermediate compound in the samples on the time of oxidation, reduction, and reoxidation. ○ series I of experiments; □ series II of experiments.

results in the equilization of the concentrations of both metals in the surface layer and in the bulk. In the meantime I.C. segregated in the bulk during the oxidation period vanishes. If, however, the reduction is continued, the fact that the outflow of vanadium from the surface toward the bulk is faster than the outflow of molybdenum results in enough enrichment of the molybdenum surface layers that segregation of I.C. occurs again. The reversibility of such effects observed in the series II of experiments is also in good agreement with the proposed model.

The effects observed in the course of the present investigation indicate that if vanadium–molybdenum catalyst is used for some catalytic processes the change in the atmosphery may result also in the change of the phase composition of the surface layers.

Acknowledgments

We would like to thank Professor D. A. Bielański for useful discussion and helpful suggestions during the preparation of this manuscript and Dr. L. Dergiel for her assistance during X-ray measurements.

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