

NOTES

Segregation in Vanadia-Molybdena Catalysts in the Course of Oxidation and Reduction Processes

Vanadia-molybdena catalysts for the oxidation of benzene to maleic anhydride are known to change markedly their chemical and phase composition in the course of their interactions with gaseous reagents and to establish a stationary state. This is due both to changes in the solid state solubility of MoO_3 in vanadium oxides and to changes in the oxidation state of both metals. A solid solution of MoO_3 in the V_2O_5 phase at the eutectic temperature (610°C) contains about 30 mole% MoO_3 . However, at temperatures below 500°C the solubility decreases to values between 10 and 15 mole% MoO_3 (1). For example, samples containing 25 to 30 mole% MoO_3 , obtained by the rapid cooling of the melt, initially forming only a solid solution undergo a segregation in the course of annealing at 400 to 500°C with the formation of the intermediate compound $\text{V}_9\text{Mo}_6\text{O}_{40}$, while the V_2O_5 phase becomes less rich in molybdenum. No such segregation occurs with samples containing less than 10 mole% MoO_3 .

However, electrical conductivity measurements of such samples as well as the changes occurring in their properties after storage at room temperature seem to indicate that in such samples the solid-state transformations which take place depend mainly on the atmosphere. We therefore decided to study these supposed processes using X-ray microprobe analysis and to check whether they are connected with any segregation of vanadium and molybdenum

occurring under the influence of the oxidizing and reducing agents. This investigation led us to the view that both processes may result in a change of the V/Mo ratio in the external layers of the crystallites. The purpose of the present Note is to describe this effect.

A sample (A) containing 10 mole% of MoO_3 and 90 mole% of V_2O_5 was obtained by fusion of an appropriate mixture of oxides at 700°C in a quartz tube. The melt was kept for 2 h at this temperature and then cooled to room temperature ($2.5^\circ/\text{min}$). The sample was a solid solution of MoO_3 in a V_2O_5 phase in which the amount of the solute was at each temperature below the solubility limit. A second sample (B) containing 30 mole% MoO_3 was obtained in the same way. The $\text{V}_2\text{O}_5/\text{MoO}_3$ ratio in this catalyst was close to the ratio existing in the most frequently used industrial catalysts. It has been shown that during prolonged annealing at 400 to 550°C sample B separated a certain amount of $\text{V}_9\text{Mo}_6\text{O}_{40}$ from the solid solution. It has also been shown previously (2) that $\text{V}_2\text{O}_5\text{-MoO}_3$ obtained by fusion always contains a certain amount of V^{4+} . This is demonstrated by the following equation using Kröger-Vink symbols:



From the data given in Ref. (2) one can estimate that sample A contained about 5 and sample B about 9 mole% V_2O_4 .

For quantitative X-ray microprobe analysis all samples must exhibit an optically flat surface. In order to fulfil this condition a small polished quartz plate was inserted into the oxide melt. It could easily be detached after solidification, leaving a flat surface. The samples of approximate size $7 \times 7 \times 3$ mm could be transferred from a scanning microscope to a reaction chamber and vice versa. A few scratches were made on the surface of each sample with a fine surgical needle, which helped us to find under the microscope the position of a crystallite chosen for an X-ray microprobe analysis. On the surface of each crystallite three spots were selected at which analysis was performed: first before the treatment of the sample; second, after oxidation carried out in air at 450°C for 141 hr; and third, after reduction with benzene vapor at 450°C for 3.5 hr. The exact positions of these spots were determined each time by means of scanning electron microscope photographs taken at the preceding stage of the experiment and also by measuring their positions with respect to some characteristic points (corners or edges of crystallites) on the image of the sample in a scanning microscope. At each selected spot at each particular stage of the experiment 10 quantitative determinations of vanadium and molybdenum were carried out using an IXA 50A X-ray microprobe. The results were consistent. The energy of the incident electron beam was 25 keV in all cases. V_2O_5 and MoO_3 samples prepared in the same way as the investigated samples were used as standards. The X-ray quanta of K_α radiation of Mo and V atoms emitted by the sample and standards from the selected spots were registered with a proportional counter. The concentrations of vanadium and molybdenum were calculated with the use of an ODRA 1325 computer. A program written by Dr. M. Łagan was used. This program contains "corrections" for the primary generation ("atomic number cor-

rection") and absorption and for fluorescence caused by characteristic lines (according to Reed (3)).

Figure 1a shows as an example a crystallite of the solid solution of MoO_3 in V_2O_5 chosen at the surface of sample A for the purpose of carrying out the experiments. Spots 1, 2, and 3 were chosen for analysis. Figure 1b shows qualitatively the distribution of molybdenum in the same crystallite before the oxidizing and reducing treatments. It can be seen that the distribution of molybdenum over the surface was practically homogeneous, and as Fig. 1c shows, this homogeneity did not suffer any dramatic changes in the course of oxidation and reduction of the sample.

The results of an X-ray microprobe point analysis at various stages of the experiments are given in Table 1. It is seen that in both samples the oxidation resulted in a decrease of the Mo/V ratio in the outer layers of the crystallites from which X-ray signals were emitted ($\sim 1.5 \mu\text{m}$ deep). For sample B the decrease is much smaller, and this is most probably connected with the simultaneous "volume segregation" due to separation of $\text{Mo}_6\text{V}_9\text{O}_{40}$ from the saturated solid solution (1). As a result the relative concentration of molybdenum in the deeper layers of the crystals (which were about $10\text{--}15 \mu\text{m}$ thick, as determined after the whole series of experiments) must have increased.

The reduction of the samples caused an opposite effect: The proportion of molybdenum increased strongly in the outer layers and the bulk was impoverished in this element.

Our results prove that both oxidation and reduction of $\text{V}_2\text{O}_5\text{--MoO}_3$ solid solutions may cause the segregation of both elements between the outer layers and the bulk of crystallites. Such effects may be explained if we assume that oxidation is accompanied by the incorporation of oxygen into the oxide lattice and formation of new crystal layers at the surface. Such a process must



FIG. 1. Electron probe microanalysis of V_2O_5 catalyst containing 10 mole% MoO_3 . (a) Electron image of the sample (Compo). 1, 2, and 3 signify spots chosen for the quantitative X-ray microanalysis; (b) Mo analysis of the same area in a fresh catalyst; (c) the same as (b) but after a cycle of oxidizing and reducing treatments.

be necessarily accompanied by the diffusion of cations from the bulk towards the surface. If the rate of diffusion of vanadium is higher than that of molybdenum this new layer will contain a smaller amount of molybdenum. Similar processes were observed in the course of oxidation of alloys composed of metals forming isomorphous oxides.

In the case of reduction oxygen is removed from the external layers of the crystal and the excess of cations must diffuse inwards. A faster diffusion of vanadium results now in a relative enrichment of the outer layers in molybdenum.

Najbar and Nizioł (4) carried out an analogous series of experiments using X-ray phase analysis of a powdered sample of

V_2O_5 - MoO_3 containing 7 mole% MoO_3 and stated that the oxidation resulted in the formation of the intermediate compound. Its amount decreased distinctly at initial stages of reduction, but the prolongation of this process resulted in its reappearance. These results correlate closely with those presented here and may be explained if we assume that in the course of oxidation the concentration of molybdenum in the inner layers becomes higher than the solubility limit of MoO_3 in V_2O_5 . In this case $V_9Mo_6O_{40}$ would be formed in the bulk of the crystal grains. In the course of reduction the enrichment of the inner layers in vanadium must at first contribute to the dissolving of the intermediate compound in an V_2O_5 phase. However, pro-

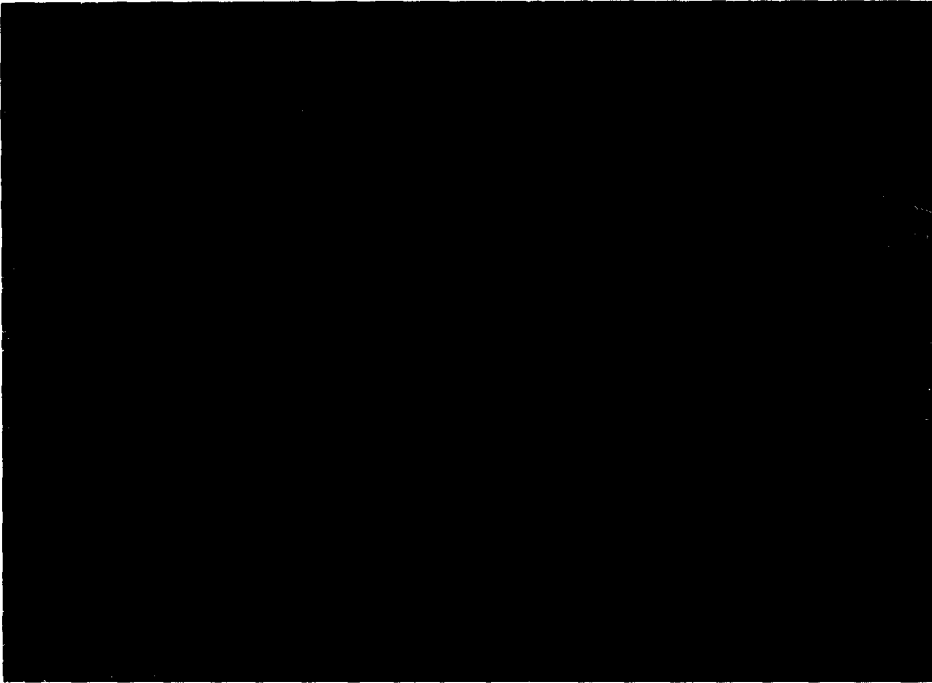


FIG. 1—*Continued.*

TABLE 1
X-Ray Microprobe Point Analysis of
MoO₃-V₂O₅ Samples

Sample ^a	Site	$N_{\text{Mo}}/N_{\text{V}}$		
		Fresh sample	After oxidation	After reduction
A	1	0.036	0.025	0.064
	2	0.049	0.028	0.062
	3	0.047	0.024	0.060
B	1	0.082	0.081	0.145
	2	0.084	0.078	0.117
	3	0.104	0.082	0.140

^a Sample A: 10 mole% MoO₃-90 mole% V₂O₅;
Sample B: 30 mole% MoO₃-70 mole% V₂O₅.

longation of this process leads to the accumulation of molybdenum in the surface layers. This results in the exceeding of the solubility limit and in the repeated separation of V₉Mo₆O₄₀ phase, this time occurring in the surface layers of the crystallites.

This segregation of vanadia and molybdena is, according to our interpretation, a kinetic effect and in principle might vanish after a long enough period of annealing of the sample in a neutral atmosphere in which no further changes in oxidation state would occur. It may appear, for example, as a transitory effect if the conditions in which a catalyst is working are suddenly changed. It seems also that the enrichment of the surface layer in molybdenum may

be the first step towards a deeper reduction of V₂O₅-MoO₃ solid solution which is interesting from the point of view of investigating the catalyst composition at the stationary state.

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