Journal of Thermal Analysis, Vol. 31 (1986) 761–771

THERMAL STABILITY AND PHASE TRANSFORMATIONS IN A COMMERCIAL VANADIA-MOLYBDENA ALKALI-PROMOTED CATALYST

R. Dziembaj, S. Hodorowicz and *G. Ciembroniewicz*

INSTITUTE OF CHEMISTRY, JAGIELLONIAN UNIVERSITY, KARASIA 3,
30—060 KRAKÓW, POLAND

(Received December 5, 1984; in revised form October 30, 1985)

Temperature-programmed decomposition, thermal analysis, thermogravimetry and high-temperature X-ray analysis have been used to investigate a commercial catalyst for the selective oxidation of benzene into maleic anhydride. It was shown that phase transformations took place in the vanadia-molybdena alkali-promoted catalyst. The transformations were caused either by high-temperature treatment or by catalytic work in an industrial plant. As a result, the β-bronze phase was formed. In the high-temperature region a reversible transformation of the bronze phase was observed. This was interpreted as the $\beta \rightleftharpoons \beta'$ phase transformation.

The catalysts which mainly contain vanadium oxide, known as V_2O_5-catalysts, give attractive selectivity in the oxidation of aromatics and alkenes to acid anhydrides or aldehydes. This has been related to the mobility of oxygen in the vanadium pentoxide lattice [1]. The temperature-programmed decomposition of V_2O_5 has shown two kinds of lattice oxygen evolution [2—3]. The first causes the formation only of an anionic vacancy solution, while the other involves a phase transformation and V_6O_{13} appears as a shear structure of V_2O_5 [4].

It is well known that alkali metal salts are often added as promoters to vanadium catalysts. Consequently, the formation of vanadium bronzes in the course of long work with the catalyst in an industrial plant seems very plausible.

There are a few reports on the catalytic activity of vanadium bronzes. Chakrabarty *et al.* [5, 6] showed that α- and β-vanadium bronzes are active in the decomposition of isopropanol. Anstadt [7] found that alkali metal vanadium bronzes are selective catalysts for the ammoxidation of alkylaromatics into nitriles.

The present work was initiated in an attempt to understand the differences and the similarities between the catalytic and related behaviour of simple vanadium

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

oxides and commercial alkali-promoted catalysts. The paper describes a study of the thermal stability and phase transformations in the catalyst KMD-219 [8] at high temperatures.

Experimental

Material

KMD-219 is a commercial catalyst applied in the selective oxidation of benzene into maleic anhydride. The catalyst was produced by the calcination of α-Al_2O_3 grains which had been saturated with a solution of ammonium vanadate and molybdate containing alkaline promoters [8]. The studies were performed on both the fresh catalyst and its "after-work" form. The latter sample was removed from the upper part of a catalyst layer which had been working for 18 months without loss of catalytic activity in an industrial plant.

Measurements

Vacuum thermal decomposition experiments were carried out using the previously-described apparatus [9]. The gaseous products were analyzed with a quadrupole mass spectrometer (QSM-200, OBREP, Warsaw) placed between a quartz reactor and a high-vacuum pumping system. The samples were heated or cooled at the constant rates of 1.2, 3.0 or 6.4 deg/min.

Due to the high sensitivity of mass spectrometric analyses, the temperature-programmed decomposition (TPD) experiments were carried out on 1, 2 or 3-grain samples. For the other techniques applied we had to use much larger samples. This was performed by scraping the "active phase" from the catalyst grains, and using such powders in the X-ray, chemical, TG and DTA analyses.

The thermogravimetric and DTA measurements were performed in a dry air stream (4 l/hr) with the aid of a Mettler Thermoanalyser-2 within the temperature range 300–900 K. Samples of 0.3 g of the "active phase" in recrystallized Al_2O_3 crucibles were heated at a constant rate of 5 deg/min to 900 K, and then cooled slowly to room temperature.

The melting points of the samples were determined under a Boetius microscope (VEB Wägetechnik, DDR).

X-ray studies were carried out on a DRON-2 (USSR) diffractometer equipped with a high-temperature UWD–2000 camera. Copper $K\alpha$ radiation, with a nickel filter, was used. The measured samples were kept at the given temperature for about 20 min before the recording of the diffraction pattern.

The products of the heating process were additionally subjected to X-ray powder diffraction analysis in a 100-mm evacuated Guinier-Hägg camera equipped with a quartz monochromator to provide clean CuK_α radiation. Platinum powder (a = 3.9238 ± 0.0003 Å, 293 K) was used as an internal standard.

The lattice parameters were calculated by least squares methods on a CDC CYBER computer.

Results and discussion

Preliminary outgassing shows that the fresh catalyst contains residual ammonium cations. This residue is removed as products of ammonia oxidation (nitrogen and nitrogen suboxide) by prolonged heating above 700 K. This is in full agreement with previously observed difficulties in obtaining a totally deammonated oxide system through the thermal decomposition of ammonium vanadates [10] and molybdates [9].

The "after-work" catalyst does not contain any traces of NH_4^+, owing to 18 months of catalytic work at about 650 K. Its surface, however, is partially covered by benzene molecules, which begin desorbing in vacuo at above 550 K and oxidizing at above 650 K. In vacuo, C_6H_6 is oxidized by the catalyst, with evolution of CO_2, CO and H_2O. Only traces of maleic anhydride are observed under such conditions.

The reduction degree (R) of KMD–219 is characterized by the number of $KMnO_4$ mval exhausted to titrate 1 g of the catalyst "active phase". The initial value of R is 1.80, and it increases because of either catalytic work (R = 2.54) or heating (6 deg/min) in an argon stream up to 900 K (R = 2.45). In both cases the NH_4^+ residue is simultaneously removed from the catalyst. Heating of the "after-work" catalyst in an argon stream cause no change in R.

The results on the limited thermal decomposition of KMD-219 are unexpected. The fresh catalyst, after the deammonation procedure (750 K, 4 h in vacuo), shows a particular variability of the lattice oxygen evolution. Initially, the partial decomposition of KMD-219 takes place at above 900 K, with an activation energy of 430 ± 30 kJ/mol (Fig. 1).

In the next temperature-programmed decomposition (TPD) run deviation from linearity is observed, and this increases up to about the fifth run, when the shape of the TPD curve is fixed (Fig. 2). In the course of the following TPD runs it was checked up to the 20th, no additional change in shape of the Arrhenius curves has been noticed. It should be added that to avoid the influence of advancing thermal decomposition, after each foregoing TPD run the catalyst has been reoxidized in the controlled way to keep the R-value constant (R = 2.50 ± 0.05).

In spite of a small hysteresis, the TPD curve is reversible; cooling also causes the

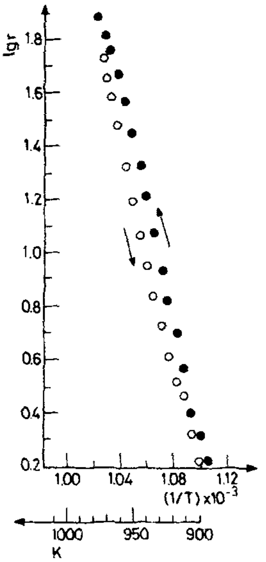

Fig. 1 Arrhenius' plot of the oxygen evolution rate measured in arbitrary units (intensity of mass-peak 32) for the first TPD run carried out upon the deammonated fresh catalyst grain. Full circules represent values taken while the temperature increases, the open ones—while the temperature decreases

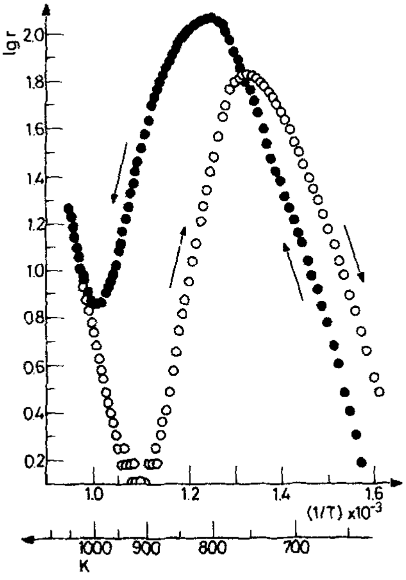

Fig. 2 Arrhenius' plot for the fifth TPD run carried out upon the fresh catalyst grain. The arrows indicate direction of the temperature variations

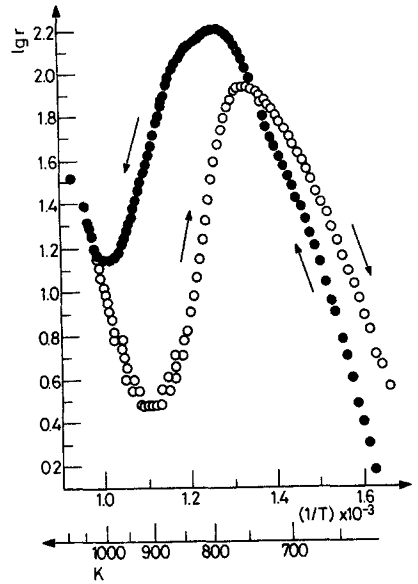

Fig. 3 Arrhenius' plot for the second TPD run carried out upon the "after work" catalyst grain. The arrows indicate direction of the temperature variations

appearance of a maximum in the curve. Thus, there are two kinds of oxygen evolution: a low-temperature form with an activation energy of about 120 kJ/mol, and a high-temperature one with E = 210 kJ/mol. Within the intermediate region 770–900 K, a solid-phase transformation or reaction should take place to result in such changes in rate of the lattice oxygen removal. In the lower-temperature region there is a phase with easily available oxygen, but in the higher-temperature region there is only a phase evolving oxygen with an activation energy about 2 times greater.

The similar experiments with the "after-work" catalyst show (Fig. 3) the evolution of two kinds of oxygen from the second TPD run, with similar activation energies as in the above example: 130 and 220 kJ/mol. Hence, it can be concluded that a similar or the same type of phase transformation takes place in the "after-work" catalyst.

Further information on the thermal instability of the catalyst is given by thermal analysis and thermogravimetry. The deammonated fresh catalyst shows two overlapping endothermic effects (Fig. 4). The first effect begins at 800 K and the second one at above 849 K. Correspondingly, in the course of linear cooling there are two exothermic effects. They are better separated, with maxima at 853 K and 802 K, than in the TPD measurements within the same temperature region. The "after-work" samples exhibit the same thermal effects in the DTA curve, but somewhat less distinctly (Fig. 5).

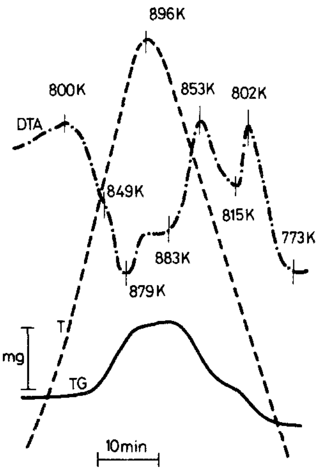

Fig. 4 DTA and TG analysis of the deammonated fresh catalyst sample in dry air stream; heating and cooling rate = 5 deg/min; initial mass = 300 mg

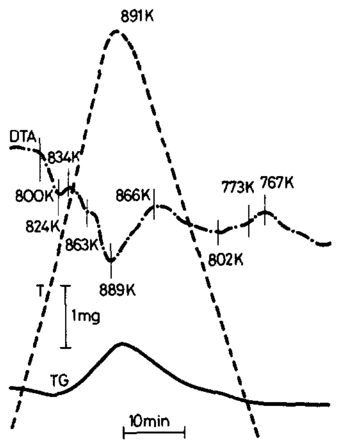

Fig. 5 DTA and TG analysis of the "after-work" catalyst sample in dry air stream; heating and cooling rate = 5 deg/min; initial mass = 300 mg

Moreover, the thermogravimetric (TG) measurements show that all catalyst samples, both fresh and "after-work", are oxidized during heating and reduced partially decomposed during cooling regardless of the atmosphere (Figs 4 and 5). Such properties are well known in the case of the melting and crystallization of vanadium bronzes [11].

To elucidate what kind of crystal transformation takes place in the catalyst, high-temperature X-ray analysis was carried out. The fresh catalyst gives a diffraction pattern with some broad lines which correspond to those of vanadium pentoxide. The samples of the "after-work" catalyst and the fresh catalyst heated previously at 950 K gave identical diffractograms. These were indexed on the basis of a monoclinic lattice with parameters very close to those of β-type bronze, $Na_{0.33}V_2O_5$ (see Table 1). The spacing of the lattice planes and the corresponding Miller indices are given in Table 2.

The diffraction patterns obtained in the temperature range 293 to 573 K did not show significant changes. The lattice constants obtained from these measurements are given in Table 1. At higher temperature, anomalous variations of the lattice constants have been noticed (see Fig. 6). This temperature coincides with the temperature at which the evolution of oxygen begins in vacuo. In the range 673–823 K (where the evolution of oxygen decreases) the X-ray diffraction patterns are similar to the low-temperatures ones, but differ in the appearance of five additional maxima with d values of 0.6 940, 0.5 126, 0.4 164, 0.3 347 and 0.2 927 nm, respectively. These lines are weak and they could not be indexed on the basis of β-phase lattice parameters. The thermal expansion in the range 823–873 K is accompanied by a strong relative change in the intensities of the reflections. At a temperature of about 900 K the sample melts. The last premelting and melting effects are correlated to the evolution of the high-temperature form of oxygen (Figs 2 and 3) and the strong endothermic effects in the DTA curves (Figs 4 and 5).

To summarize, it can be concluded that the working of the commercial catalyst KMD–219 in an industrial plant is accompanied by the appearance of vanadium bronzes in the catalyst. Although the temperature in the industrial reactor was kept at 650 K, due to the high oxidation heat and the thermal insulator properties of the vanadia catalyst, some local overheating could not be excluded. The time factor, 18 months in the industrial plant, should also be taken into account.

Table 1 Lattice parameters and unit cell volumes of β-type vanadium and mixed molybdenum-vanadium bronzes as well as KMD–219 catalyst

Sample and source	Temp., K	Lattice parameters, nm				Volums V, nm³	V, %
		a	b	c	β		
$Na_{0.33}V_2O_5$ (22)	293	1.008	0.361	1.544	109.6	0.5293	
$Na_{0.33}V_2O_5$ (23)	293	1.00393	0.36053	1.53353	109.205	0.5241	
mixed bronze (24)	293	1.55006	0.36722	1.01926	109.185	0.5479	
KMD–219	293	1.55591	0.36531	1.01631	108.996	0.5462	0
(present work)	473	1.55814	0.36534	1.01754	109.034	0.5475	0.24
	573	1.56094	0.36541	1.01902	109.034	0.5494	0.58
	673	1.56401	0.36662	1.02071	109.061	0.5532	1.28
	773	1.56482	0.36602	1.02103	109.112	0.5525	1.15
	823	1.56413	0.36542	1.02052	109.101	0.5511	0.89
	873	1.57221	0.36653	1.03164	109.453	0.5605	2.62

Table 2 Powder diffraction pattern of the "after work" catalyst and the reference material

Observed pattern				β-$Na_{0.33}V_2O_5$ (according [25])		
d_{obs}, nm	d_{calc}, nm	I_{obs},*	*h k l*	d_{obs}, nm	I_{obs}	*h k l*
1	*2*	*3*	*4*	*5*	*6*	*7*
0.9612	0.9609 0.9602	35	0 0 1 1 0 $\bar{1}$	0.946	s	1 0 0
0.7363	0.7356	50	2 0 0	0.728	s	0 0 2
0.7060	0.7062 0.7053	8	1 0 1 2 0 $\bar{1}$	—	—	—
0.4810	0.4805 0.4801	25	0 0 2 2 0 $\bar{2}$	0.472	m	2 0 0
0.3889	0.3886 0.3883	10	3 0 1 4 0 $\bar{1}$	0.385	mw	$\bar{1}$ 0 4
0.3676	0.3678	15	4 0 0	0.362	mw	0 0 4
0.3540	0.3545 0.3531	20	1 1 0 2 0 2	0.347	mw	2 0 2
0.3521	0.3525	6	4 0 $\bar{2}$	—	—	—
0.3416	0.3415 0.3414	100	0 1 1 1 1 $\bar{1}$	0.337	vs	$\bar{1}$ 1 1
0.3244	0.3245	25	1 1 1	0.320	ms	$\bar{1}$ 1 1
0.3205	0.3203 0.3203	8	0 0 3 3 0 $\bar{3}$	—	—	—
0.3110	0.3113 0.3111	70	4 0 1 5 0 $\bar{1}$	0.306	s	1 0 4
0.2934	0.2937 0.2934	80	1 0 3 4 0 $\bar{3}$	0.292	ms	$\bar{3}$ 0 4
0.2752	0.2752 0.2750	50	1 1 $\bar{2}$ 3 1 $\bar{2}$	0.272	ms	$\bar{2}$ 1 3 2 1 1
0.2661	0.2662	13	3 1 1	0.263	w	1 1 3
0.2548	0.2548	18	4 0 2	—	—	—
0.2474	0.2475	18	1 1 $\bar{3}$	0.2445	w	$\bar{3}$ 1 1
0.2405	0.2407 0.2402 0.2401	20	3 1 $\bar{3}$ 0 0 4 4 0 $\bar{4}$	0.2371 0.2257	w w	4 0 0 $\bar{4}$ 0 4
0.2353	0.2354 0.2351	5	3 0 3 6 0 $\bar{3}$	—	—	—
0.2290	0.2291 0.2289	25	5 1 0 1 1 3	—	—	—

Table 2 cont.

Observed pattern				β-$Na_{0.33}V_2O_5$ (according [25])		
d_{obs}, nm	d_{calc}, nm	I_{obs},*	*h k l*	d_{obs}, nm	I_{obs}	*h k l*
1	*2*	*3*	*4*	*5*	*6*	*7*
0.2211	0.2210 0.2209	31	6 0 1 5 0 2	0.217	ms	?
0.2092	0.2092	8	2 0 4	—	—	—
0.19912	0.19908	28	1 0 $\bar{5}$	0.197	m	?
0.19430	0.19430	8	6 0 2	—	—	—
0.19211	0.19219 0.19201	6	0 0 5 1 1 4	—	—	—
0.18900	0.18900	15	7 1 $\bar{1}$			
0.18268	0.18265	50	0 2 0	0.1806	ms	?

* The observed intensity is the average of two independent measurements.

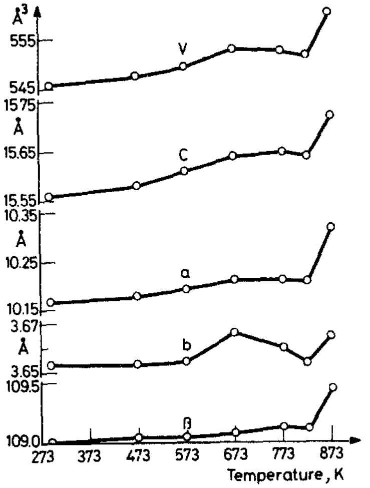

Fig. 6 Variation of lattice parameters (*a*, *b*, *c* and *β*) and unit cell volume (*V*) of the "after-work" catalyst with temperature; (1 Å = 10^{-10} m)

Unfortunately, to this time there is no unanimous opinion concerning the processes in vanadia bronzes at high temperatures. It is known that the formation of Na–V bronze is accompanied by the evolution of a noticeable amount of oxygen [11–13]. According to Fotiev *et al.* [14–15], the effect can be observed at a temperature higher than 613 K and under atmospheric conditions.

From the other side, in the temperature range 673–873 K some authors have observed anomalies in the physical properties [16–17]. Kapustkin [18] explained this by the occurrence of a semiconductor metal phase transformation and discussed this process within the framework of a Mott model.

Recently, Volkov *et al.* [19] investigated a phase transformation in β–Li–V bronze in this range of temperature.

The results of their thermal analysis and X-ray investigations are very similar to those described by us. They postulated a phase transformation accompanied by a redistribution of lithium ions among the possible positions in the crystal lattice.

This process is very plausible from a structural point of view. In the crystal structure of the β-vanadium bronzes, the M^+ ions randomly occupy two positions within tunnels, with different coordinations and consequently with different bond energies [20]. Elevation of the temperature leads to a redistribution of the M^+ ions among the possible positions, and as a result microregions of the vanadium oxide bronze β'–$M_xV_2O_5$ are formed. Macroscopically, this is manifested by new diffraction maxima. This transformation is reversible if the heating-cooling cycle is carried out.

In our case, the object of study was an industrial catalyst. Such a catalyst is usually referred to as a "vanadia-promoted", or more precisely a "vanadia-molybdena alkali-promoted catalyst". The solubility of molybdenum oxide in the V_2O_5 lattice is enough to form a solid solution up to $Mo/V = 0.2$, whereas at higher molybdenum concentrations the intermediate compound $V_9Mo_6O_{40}$ is formed [21]. Both these phases were detected by electron diffraction experiments in the fresh catalyst; work with the catalyst causes some loss of molybdenum content.

Our present high-temperature X-ray analysis indicates that the predominant phase in the after-work catalyst is undoubtedly β-vanadium-molybdenum bronze, $Na_xV_{2-y}Mo_yO_5$ ($y = 0.347$). The crystal structure of this bronze and its domain in the $V_{2-y}Mo_yO_5$ versus $Na_xV_2O_5$ diagram were determined by Hagenmuller *et al.* [25].

References

1 A. Bielański and J. Haber, Catalysis Rev.—Sci. Eng., 19 (1979) 1.

2 R. Dziembaj, React. Kinet. Catal. Lett., 9 (1978) 389.

3 R. Dziembaj, G. Ciembroniewicz and R. Kalicki, ibid., 12 (1979) 89.

4 R. Dziembaj and J. Piwowarczyk, J. Solid State Chem., 21 (1977) 387.

5 D. K. Chakrabarty, D. Guha and A. B. Biswas, ibid., 22 (1977) 263.

6 D. K. Chakrabarty, D. Guha, I. K. Bhatnagar and A. B. Biswas, J. Catal., 45 (1976) 305.

7 H. P. Anstadt, Canadian Pat., 1, 072, 580.

8 Polish Pat. 100, 811.

9 G. Ciembroniewicz, R. Dziembaj, and R. Kalicki, J. Thermal Anal., 27 (1983) 125.

10 L. Dziembaj and R. Dziembaj, ibid., 17 (1979) 57.

11 W. Prandtl and H. Murschhauser, Z. Anorg. Allgem. Chemie, 56 (1908) 173, ibid. 60 (1908) 441.

12 R. P. Ozerov, Zh. Neorg. Khim., 4 (1959) 1047.
13 B. V. Slobodin and A. A. Fotiev, Zh. Prikl. Khim., 38 (1965) 801.
14 V. L. Zolotavin, L. K. Tolstov, A. A. Ivakin, A. A. Fotiev, V. V. Mochalov and Yu. F. Bukreev. Izv. Akad. Nauk SSSR, Ser. Neorg. Mater., 3 (1967) 160.
15 A. A. Fotiev, E. D. Pletneva and M. Ya. Khodos, Zh. Neorg. Khim., 26 (1981) 3186.
16 Z. I. Ornatskaya, Fiz. Tverd. Tela, 6 (1964) 1254.
17 I. H. Perlstein and M. I. Sienko, J. Chem. Phys., 48 (1968) 174.
18 A. A. Fotiev, V. L. Volkov and V. K. Kapustkin, in Vanadium Oxide Bronzes, Izd. Nauka, Moscow 1978, p. 126.
19 V. L. Volkov and P. Ya. Novak, Zh. Neorg. Khim., 27 (1982) 1658.
20 J. Galy, J. Darriet, A. Casalot and J. B. Googenough, J. Solid State Chem., 1 (1970) 339.
21 A. Bielański, R. Dziembaj, K. Dyrek and E. Wenda, Comm. Depart. Chem. Bulg. Acad. Sci., 6 (1973) 531.
22 A. D. Wadsley, Acta Crystallogr., 8 (1955) 695. 695.
23 R. P. Ozerov, G. A. Goler and G. S. Zhdanov, Kristallografiya, 2 (1957) 217.
24 J. Darriet, J. Galy and P. Hagenmuller, J. Solid State Chem., 3 (1971) 604.
25 N. S. Butt, A. Fish and F. Z. Saleeb, J. Catalysis, 5 (1966) 494.

Zusammenfassung — Temperaturprogrammierte Zersetzung, Thermoanalyse, Thermogravimetrie und Hochtemperatur-Röntgenanalyse wurden zur Untersuchung eines kommerziellen Katalysators für die selektive Oxydation von Benzol zu Maleinsäure herangezogen. Es wird gezeigt, daß in dem einen Alkalipromotor enthaltenden Vanadinoxid-Molybdänoxid-Katalysator Phasenübergänge vor sich gehen. Die Phasenübergänge, als deren Ergebnis eine β-Bronzephase gebildet wird, wurden entweder durch Hochtemperaturbehandlung oder durch sich in einer industriellen Anlage während des Betriebes abspielenden Vorgänge verursacht. Im Bereich hoher Temperaturen wurde eine reversible Umwandlung der Bronzephase beobachtet, die als $\beta \rightleftarrows \beta'$ Phasenübergang interpretiert wurde.

Резюме — Температурно-программированное разложение, термический анализ, термогравиметрия и высокотемпературный рентгеноструктурный анализы были использованы для исследования выпускаемого промышленностью катализатора для селективного окисления бензола до малеинового ангидрида. Показано, что ванадий-молибденовый катализатор, промотированный щелочными металлами, подвергается фазовым переходам. Такие фазовые переходы, вызываемые высокотемпературной обработкой этого катализатора или же работой его в технологических условиях, всегда приводили к образованию β-бронз. В области высоких температур наблюдалось $\beta \rightleftarrows \beta'$ фазовое превращение бронз.