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IV RUSSIAN CONFERENCE WITH THE PARTICIPATION OF CIS COUNTRIES ON THE SCIENTIFIC BASES OF CATALYST PREPARATION AND TECHNOLOGY

Reasons for the Deactivation of Vanadia–Titania Catalysts for Partial Durene Oxidation during Prolonged Performance

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Abstract—The catalytic properties of vanadia–titania catalysts and the reasons for their change in the course of durene oxidation to pyromellitic dianhydride are studied. The catalysts differ in preparation conditions and the composition of the active component film deposited on a nonporous support. The stability of the catalytic properties in the reaction medium of durene oxidation is mainly determined by the properties of titania precursors.

INTRODUCTION

Pyromellitic dianhydride (PMDA) is a raw material for the manufacturing of polyimides with unique properties. PMDA can be prepared by heterogeneous catalytic gas-phase durene oxidation [1]. The simplest catalysts for this process are fused V_2O_5 and V_2O_5 supported on a nonporous carrier (corundum and silicon carbide). To enhance the activity and selectivity of the catalyst, the additives W, P, Sn, Ti, Ag, Mo, Cu, Na, K, Rb, and Cr have been proposed [2].

Durene oxidation to PMDA resembles *o*-xylene oxidation to phthalic anhydride over vanadia–titania systems deposited as a thin film on the surface of nonporous supports. These catalysts are the most selective and therefore recommended for PMDA synthesis [3–5].

It has been found that the structure of the active phase in the V–Ti systems depends essentially on the V_2O_5 concentration (C_V) and preparation conditions [6–17]. The presence of isolated (tetrahedrally or octahedrally coordinated) vanadium cations, cluster oxide species of various sizes, and a disperse V_2O_5 phase has been assumed. Note that the structures of model systems containing one or several layers of an active component have been described in these works, whereas the catalysts recommended for industrial use contain 5.0 to 25.0 wt % V_2O_5. In addition, data reported previously only deal with the initial state of an active component in the catalyst, and this state may change under the action of the reaction medium [18].

Our aim was to study the effect of prolonged exposure to the reaction medium in durene oxidation to PMDA on the catalytic properties, structure, phase composition, and valent state of vanadia–titania systems which differ in their composition and preparation conditions.

EXPERIMENTAL

To prepare catalysts, we used V_2O_5, aqueous solutions of NH_4VO_3 and VOC_2O_4, Ti(IV) oxide of (A1 trademark, anatase), which is used for commercial KS and KT catalysts, and hydrated titania $TiO_2 \cdot nH_2O$. Samples of film catalysts were prepared as follows. Porcelain balls with a diameter of 8 mm were placed into a heated cylinder, and suspended TiO_2 (anatase) in a VOC_2O_4 or NH_4VO_3 solution heated to 90°C was introduced by a pneumatic injector. Various concentrations of active components in the catalysts were achieved by changing the composition of the suspension. The second procedure differed only in the composition of the aqueous suspension containing V_2O_5, TiO_2 (anatase), and $TiO_2 \cdot nH_2O$ in different ratios. Only one sample prepared by sputtering the suspension of the above components with the 1 : 3 : 1 weight ratio (22 wt % V_2O_5) was studied in this work the most selective in the catalytic process. Henceforth, the samples prepared by the first method are denoted as **VT*m***, where *m* is the concentration of V_2O_5 (wt %) in the film of active components, and the samples prepared by the second method are denoted as VTG.

The weight of the film of active components was ~3% of the support weight. The samples with C_V of 3.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, and 90.0% based on the weight of the film of active components were prepared.

The samples were studied by transmission electron microscopy on a JEM-100 CX instrument with an accelerating voltage of 100 kV. Electron microdiffraction was used to determine the structural features and phase composition of particles. The specimens for obtaining microscopic patterns were prepared using alcohol suspensions by ultrasonic dispersion [19]. The surface areas of V_2O_5 were estimated by NH_3 and CO_2 adsorption in a pulse regime [20]. Preliminary experi-

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ments showed that in a pulse regime, NH_3 adsorbs at 100°C only on the surface of V_2O_5 and CO_2 adsorbs at 30°C on the TiO_2 surface. The surface area of a sample was estimated by comparing the amounts of NH_3 adsorbed on it and on V_2O_5 with the specific surface area determined by nitrogen thermal desorption.

Photoelectron spectra were recorded on an ESCA-3 instrument using AlK_α radiation without previous treatment of catalysts at a residual pressure in an analyzer chamber of 5×10^{-9} torr [21]. The ^{51}V NMR spectra were recorded at room temperature on a Bruker MSL-400 spectrometer with a frequency of 105.2 MHz at the pulse width of 1–2 μs and the number of pulses per second of 10 Hz [22]. The ESR spectra were recorded on an ER-200D spectrometer at 77 K with a frequency of 9.3 GHz (λ = 3.2 cm). Before the studies by NMR and ESR, the samples were placed in quartz tubes and treated in a helium flow at 350°C for 1 h. Then the samples were moved into quartz ampules without a contact with air, sealed, and introduced into a resonator of the spectrometer.

Before the study of the physicochemical properties, the film of active components was separated from the support.

The catalytic properties of the V/Ti catalysts in durene oxidation were studied on a laboratory flow setup with an integral reactor (catalyst volume was 15 cm^3) as well as on a pilot setup with four reaction tubes whose sizes were the same as those of the tubes of the industrial reactor (catalyst volume in one tube was 500 cm^3) placed into a salt bath [22]. This allowed the simultaneous study of four samples. The experiments were carried out at atmospheric pressure in the temperature range (T_r) of 360–480°C at a durene concentration in a durene–air mixture (C_d) of 0.15–0.17 vol % and a space velocity (V_d) of 3500–12000 h^{-1}. The above conditions were close to those of the real industrial process. The rate of non-catalytic durene oxidation was negligibly small. The composition of the oxidation products was determined by GLC using glass capillary columns. The apparent activity of the catalysts was characterized by the minimal temperature of complete durene conversion, and the selectivity of PDMA formation (S_P) was evaluated as the PDMA yield based on converted durene.

RESULTS AND DISCUSSION

As was mentioned above, the structure of the vanadia–titania catalysts depends on their composition and preparation conditions. Our results confirm this statement. Round particles with faceting are present in the sample VT1 (Fig. 1a). According to electron microdiffraction data, the particles are composed of TiO_2(anatase). The particle sizes are 30–150 nm. Uniform extinction bands give evidence for the good crystallinity of the particles. V_2O_5 particles are not seen in this sample. We suggest that vanadium oxide compounds are present in a highly dispersed state due to interaction with the surface of TiO_2. However, the limited resolution of the electron microscope prevents us from stating the formation of surface vanadium compounds with a thickness of about a monolayer. The low resolution is due to the fact that the atomic weights of vanadium and titanium are close and the ordinal numbers of these elements are small [23].

When C_V is increased to 3.0 wt %, the needle-shaped particles of the V_2O_5 phase appear (Fig. 1b). Their average length is 300 nm, and the thickness is 30–50 nm. In addition to coarse V_2O_5 species, round clusters with sizes of up to 3 nm (the largest are 20 nm in size) are seen on the surface of anatase, which also belong to the V_2O_5 phase (Fig. 2a). The size and shape of the TiO_2 (anatase) particles, as well as the needle morphology of the coarse dispersed V_2O_5 phase, are almost the same for all samples of the VT*m* series. The thickness of needles grows with an increase in C_V. Thus, the thickness of needles in the samples with low C_V is ~30 nm and increases over 300 nm in the VT60 sample (Figs. 1b–1d). The needles with greater sizes are formed due to the coalescence of fine particles into block structures.

Two types of TiO_2 particles are found in the sample prepared from a mixture of TiO_2 (anatase) and $TiO_2 \cdot nH_2O$ (series VTG) (Fig. 3a). The particles of the first type have a size of ~100 nm and those of the second type are ~20–30 nm joined into agglomerates with a size of 500 nm. Microdiffraction data show that the phase composition of the particles of both types corresponds to anatase. Similarly to the VT*m* series, the V_2O_5 particles of a needle shape with a length up to 100 nm and a width of ~30 nm are found in the samples of the VTG series (Fig. 3b). There are fewer needles and their structure is more perfect than that of the VT*m* catalysts with the same or higher C_V. In addition to the particles of the V_2O_5 phase, some particles of the VO_2 phase of a monoclinic modification (m) are seen in the samples of the VTG series.

The high dispersion of V_2O_5 in the samples with low C_V is confirmed by the data on ammonia adsorption. The surface of 1 g of V_2O_5 in the sample VT1 is larger than 200 m^2 (Fig. 4). It gradually decreases with increasing C_V and achieves the value of the surface area of powder V_2O_5 in the samples containing more than 30 wt %.

The total surface area of the film of active components passes through a maximum because of a decrease in the dispersion of vanadia compounds with an increase in the V_2O_5 content in the catalyst. In the VT*m* series, the maximum is seen on sample VT20 (Fig. 4).

Note that CO_2 adsorbs only on the surface of initial TiO_2 and samples VT1 and VT3. When taking into account that CO_2 does not adsorb on the surface of V_2O_5, one can conclude that the active component does not cover the support surface in these samples completely even at C_V that corresponds to several layers (3.0 wt %).

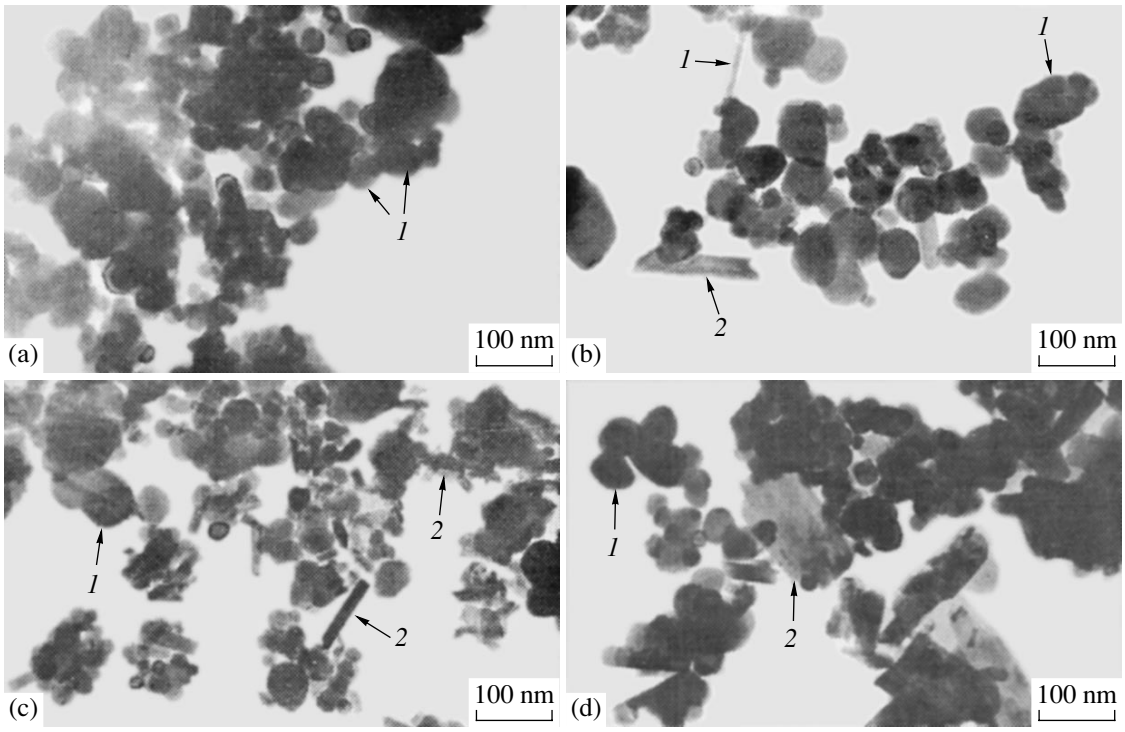

Fig. 1. Electron micrographs of initial samples of the VT*m* series with V_2O_5 content, wt %: (a) 1.0, (b) 3.0, (c) 20.0, and (d) 60.0; (*1*) particles of TiO_2, (*2*) particles V_2O_5.

The state of vanadia compounds in the samples of the VT*m* and VTG series after their long residence in the reaction medium is substantially different. The VT10 sample after operation for 1150 h contains a great amount of particles of an irregular shape with a size of ~70 nm that consist of the VO_2 (m) with the lattice parameters a_0 = 5.743 Å, b_0 = 4.517 Å, c_0 = 5.375 Å, and β = 122.6° (Fig. 2b) [24]. The structure of VO_2 is confirmed by electron microdiffraction data. Microdistortions that manifest themselves on the micrographs as curved extinction bands are typical of these particles. The particles of the VO_2 (m) phase are likely formed by the agglomeration of small crystals upon their reduction in the reaction medium.

The morphology of the particles of the VT20 sample after operation for 1150 h differs from the initial morphology in the appearance of many small particles with a size of at least 50 nm on the surface of anatase in addition to large particles of V_2O_5. The phase composition of these small particles is unknown. Apparently, these particles comprise a reduced form of VO_2 (m) as in the case of sample VT10 operated for 1150 h.

The VTG sample operated in durene oxidation for 3800 h contains mostly the V_2O_5 phase. The amount of the VO_2 (m) particles is small and slightly differs from that in the initial sample.

The ^{51}V NMR study [22, 25] of the vanadia–titania systems with low C_V (less than a monolayer coverage) revealed isolated tetrahedral vanadium complexes, which were strongly distorted because of the strong binding of vanadium to the TiO_2 surface through three oxygen atoms. The samples were prepared by the treatment of anatase with $VOCl_3$ vapor followed by the removal of physically adsorbed $VOCl_3$ and hydroxylation of unreacted V–Cl bonds. The broadened lines in the ^{51}V NMR spectrum corresponded to these complexes. Such structures were formed at low C_V and low concentrations of the hydroxyl groups on the anatase surface. At higher C_V, the above complexes likely began to associate to clusters (sites I). In parallel, clusters of less distorted tetrahedra bound to the TiO_2 surface through two oxygen atoms (sites II) formed. The signal typical of V_2O_5 appeared in the spectra at coverages higher than a monolayer.

The ^{51}V NMR spectrum of the sample with C_V = 1.0 wt % prepared from well-crystallized anatase with S_{sp} = 8.5 m^2/g (sample VT1) (Fig 5, spectrum *1*) differs significantly from the spectra of known pure compounds. The strong broadening of the spectrum does not allow the determination of the number of lines. One can suggest that the spectrum consists of one line with the parameters $\delta_1 \approx -300$, $\delta_2 \approx -500$, and $\delta_3 \approx -1000$ ppm typical of V^{5+} tetrahedral complexes that are similar to those found in [22, 25]. The high anisotropy of the spectrum is most probably due to the formation of a vanadium compound whose structure is distorted by strong binding with the TiO_2 surface.

When C_V is increased to 3.0 wt % (sample VT3), an additional band appears in the region of $\delta \approx -315$ ppm

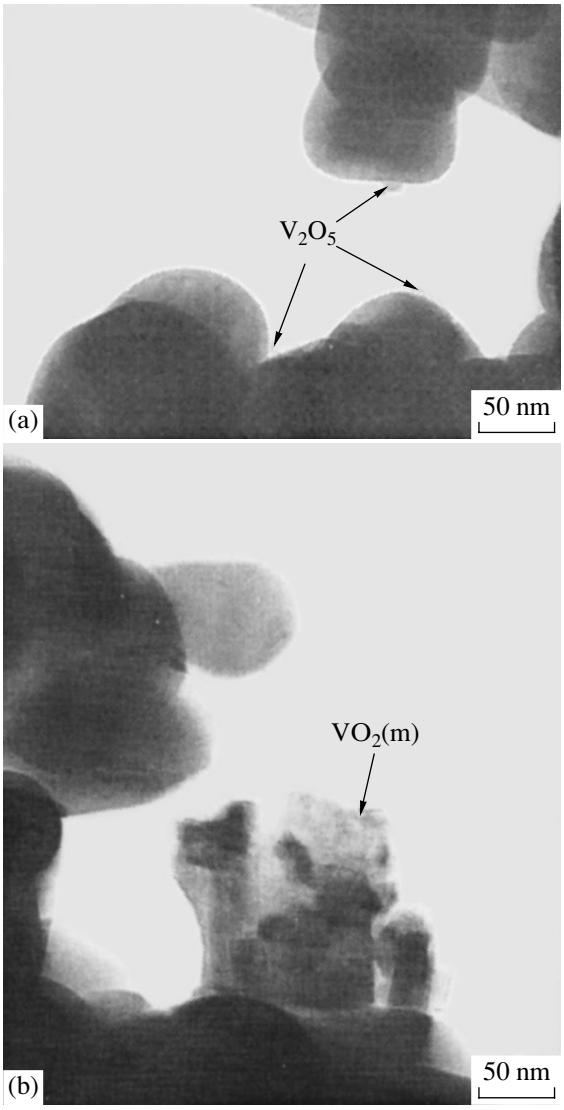

Fig. 2. Electron micrographs of sample VT10 (a) before and (b) after residence in the reaction medium for 1150 h.

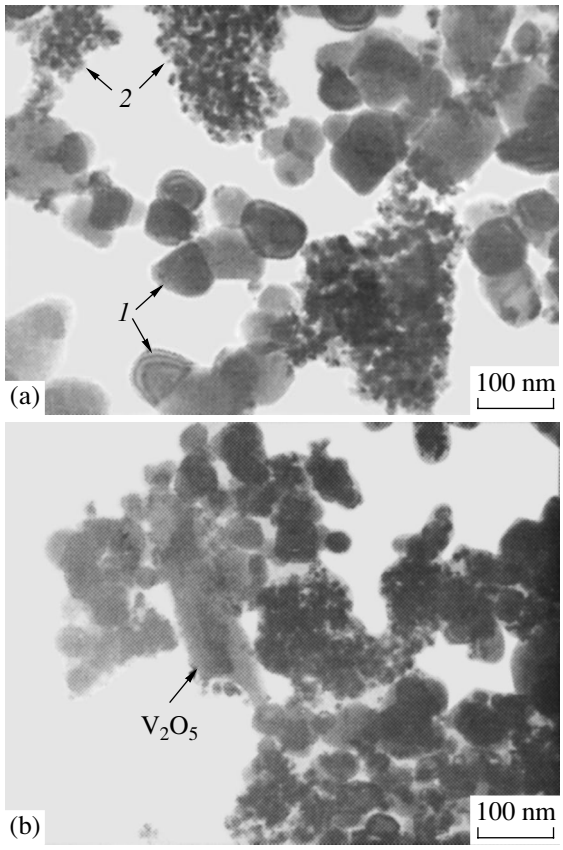

Fig. 3. Electron micrographs of the initial sample of VTG series: (a) particles TiO_2 (*1*) coarse particles of TiO_2 and (*2*) agglomerates of highly dispersed particles); (b) particles V_2O_5.

(Fig. 5, spectrum *2*). The relative contribution of this band increases with increasing C_V. In the spectrum of the initial sample VT10 (Fig. 5, spectrum *3*), the line with axial anisotropy of the chemical shift tensor ($\delta_1 \approx -315$ ppm, $\delta_2 \approx -1250$ ppm) is the most pronounced. Comparison with the spectra of known compounds [26] led us to conclude that the compound under consideration is V_2O_5. After prolonged residence of this sample under reaction conditions, the line corresponding to V_2O_5 disappears (Fig. 6) The remaining line is close in its parameters to that for a surface compound formed in the VT*m* samples with low vanadia contents (Fig. 5).

Figure 7 presents the ^{51}V NMR spectra of the VTG series sample, both initial and spent in the reaction. As can be seen, these spectra are close and correspond to the well-crystallized V_2O_5 phase (V_2O_5 ($\delta_1 \approx -315$ ppm, $\delta_2 \approx -1250$ ppm). The intensity of the spectrum of the spent sample is lower as in the VT*m* series catalysts, and the line from the surface V–Ti compound is seen in the region of –500 ppm whose relative intensity is higher in the spent sample.

Thus, one can suggest that the surface V–Ti compounds similar to sites I and II described in [22, 25] occur in our samples.

According to the XPS data, the atomic V/Ti ratio in the samples of the VTG series after prolonged residence in the reaction medium changes slightly but decreases 1.5–2.5 times in the VT*m* series samples. For example, the atomic ratio in VT3 (initial) is 0.30, in VT10 (initial) is 0.58, VT20 (initial) is 1.50, VT20 (50 h of operation) is 0.92, VT20 (1150 h) is 0.59, VT60 is 2.9, VTG (initial) is 0.64, and VTG (3800 h) is 0.59. Since the pore structure of a catalyst after prolonged action of the reaction medium remains unchanged, one can suggest that the distortion and agglomeration of the surface vanadium-containing structures change the V/Ti ratio. This conclusion is confirmed by the electron microscopy. As was mentioned above, the amount of small clusters with a size of ~3 nm decreases substantially in the spent VT10 sam-

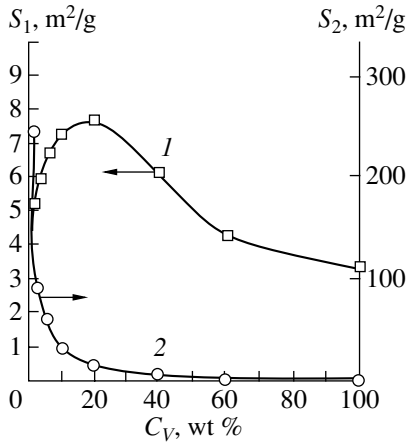

Fig. 4. The specific surface area of V_2O_5 as a function of its content: (*1*) specific surface area based on 1 g of the film of the active components (S_1); (*2*) specific surface area of V_2O_5 based on 1 g V_2O_5 (S_2).

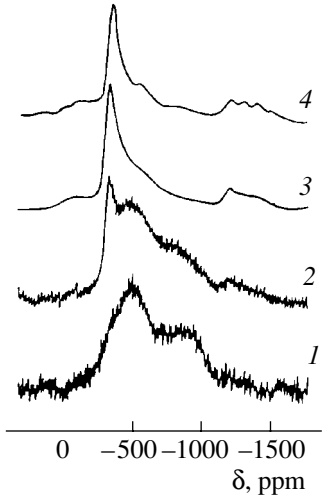

Fig. 5. The ^{51}V NMR spectra of the VT*m* samples with the V_2O_5 content, wt %: (*1*) 1.0, (*2*) 3.0, (*3*) 10.0, and (*4*) 20.0.

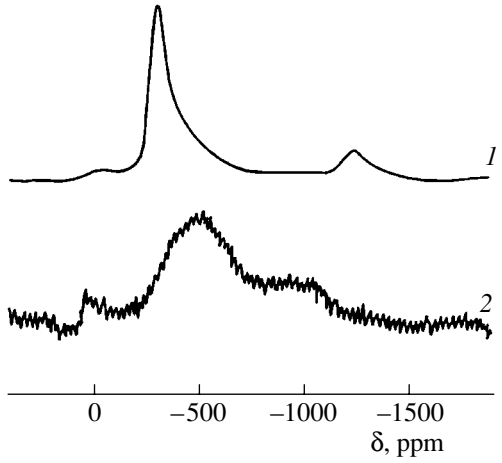

Fig. 6. The ^{51}V NMR spectra of the sample VT10 (*1*) before and (*2*) after exposure to the reaction medium for 1150 h.

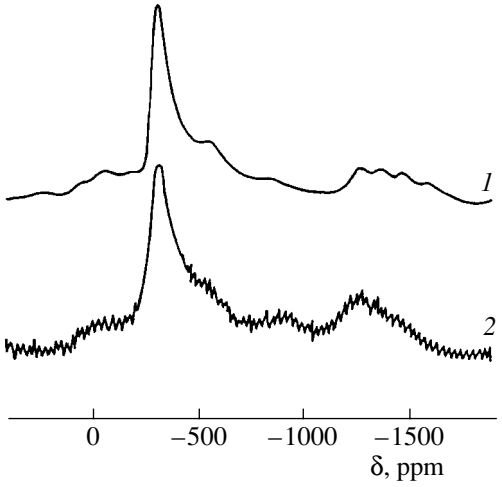

Fig. 7. ^{51}V NMR spectra of the samples of VTG series (*1*) before and (*2*) after contact with the reaction medium for 3800 h.

ple but larger (up to 70 nm) particles of V_2O_5 (m) appear.

It follows from NMR (Fig. 7), ESR, and chemical analysis data that a substantial fraction of vanadium in the stable VTG catalyst remains as V^{5+} after reaction. Note that V_2O_5 in this catalyst is reduced mainly to compounds containing vanadyl ion VO^{2+} rather than to VO_2 (m). The ESR spectrum of VO^{2+} is characterized by a hyperfine structure. Only values of $q_\perp = 1.98$ G and $b_2 = 80$ G were firmly estimated because of the overlapping of different signals.

Thus, the main reason for a change in the structure of the V–Ti catalysts of the VT*m* series is coarsening of the surface structures of the V^{5+} oxide, including the distortion of active surface compounds, which is accompanied by their complete reduction to inactive VO_2 (m).

It remains unclear why the catalysts, for example VTG and VT20, with a close chemical composition differ significantly in resistance to agglomeration and reduction. This is probably due to different preparation procedures for these catalysts. When the VTG catalyst is prepared, the support contains hydrated titania along with well crystallized TiO_2 (anatase). The hydrated titania transforms into anatase upon calcination, and the latter is seen on electron-microscopic patterns as highly dispersed particles. Due to a high content of hydroxyl groups on the surface, V^{5+} ions interact with the support to form V–Ti compounds, which cover the surface almost completely. The V^{5+} ions in the surface compound coordinate the hydroxyl groups, which interact with the deposited V^{5+} compounds to form initially disordered V_2O_5 and then, upon calcination, well crystallized V_2O_5 particles (Fig. 8, structure a).

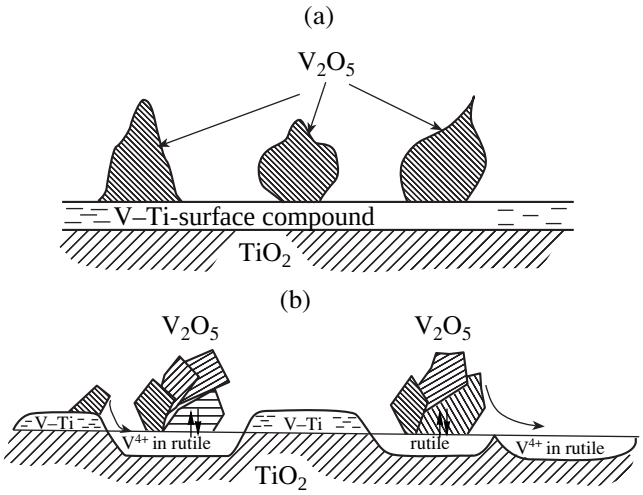

Fig. 8. Structures of catalysts (a) VTG and (b) VT*m*. Diffusion of particles to form a solid solution of V^{4+} in rutile is shown by arrows.

Such efficient interaction is absent in the case of the VT*m* catalysts. Despite the excess of V_2O_5, the active surface phase exists in the form of distinct islands on the support. According to the X-ray diffraction data, a small amount of rutile is present in the VT*m* samples. Rutile as a thermodynamically more stable phase is located mostly on the surface, and a solid solution of V^{4+} ions in rutile is formed upon the deposition of V_2O_5. Therefore, a fraction of V^{5+} in the form of surface monolayer compounds in the VT*m* samples is substantially smaller than in the VTG sample. Most of V^{5+} is distributed over the free surface as blocks of large needle crystals of V_2O_5 that are formed by the coalescence of smaller needles. In addition, the interaction between V^{5+} and the support on the interface during calcination of the sample can produce a small amount of the V^{4+} solid solution in rutile. The signals typical of the V^{4+} solid solutions in rutile were found in the ESR spectra of the initial VT*m* samples. These were lines with a hyperfine structure and the following parameters of hyperfine interaction: A = 160 G and B = 30 G. The $q_\perp$ and $q_\parallel$ values were not estimated because of signal overlap. The V^{4+} concentration was several percents of C_V. Taking into account the low specific surface areas of the BT*m* samples and the fact that the main amount of vanadium occurs as V_2O_5 large crystallites, the fraction of the surface occupied by the solid solution can reach significant values (Fig. 8, structure b).

More regular V_2O_5 particles are formed by interaction between V^{5+} and hydroxyl groups, which are nearly absent from the surface of the VT*m* samples, and hence the contribution of chemical interactions is small. Therefore, V_2O_5 is randomly distributed over the surface. Unlike VTG, the V_2O_5 crystals in the VT20 and VT60 samples has a pronounced block structure formed by the coalescence of closely located small V_2O_5 crystallites.

The agglomeration of VO_2 particles after prolonged exposure to the reaction mixture can be described as follows. The V^{4+} ions of a solid solution in rutile diffuse to the surface and serve as the centers of V(IV) crystallization to the VO_2 monoclinic structure. When V^{4+} ions move from positions typical of the rutile structure, the VO_2 (m) phase can nucleate on the TiO_2 surface. It is known that the transition from the tetragonal structure (V^{4+} in rutile) to the monoclinic one occurs readily and does not require significant lattice reconstruction [27]. This suggestion agrees with ESR data for the spent VT20 sample, which reveal a decrease in the V^{4+} concentration both in the solid solution and in the form of the isolated VO^{2+} particles. The diffusion of V^{4+} to this center is likely a rate-determining stage. Diffusion can occur more rapidly when V_2O_5 crystals are located directly on the surface region occupied by the solid solution. In addition, growing VO_2 crystals can "withdraw" the V^{4+} ions, formed during reaction, from the surface sites. This process is slower than the above process because it requires the rupture of chemical bonds.

The structure in which vanadium of the V–Ti surface compounds is bound to the support (anatase) and V_2O_5 via chemical bonds and the above centers of crystallization are absent is more stable. In this structure, V_2O_5 can partially be reduced to the equilibrium amount of VO^{2+} (under reaction conditions). Structure (a) is usually present in the VTG sample on the TiO_2 small particles that are formed from titania hydrate, and structure (b) is present in the VT*m* and VTG samples on the coarsely dispersed TiO_2 particles.

Catalytic Properties of the Vanadia–Titania Catalysts

A change in the state of a catalyst and, as a consequence, its catalytic behavior in the reaction medium is a common phenomenon in heterogeneous catalysis [18, 28, 29]. It follows from our findings that this is also characteristic of vanadium-containing catalysts in durene oxidation. For example, the activity of a sample containing only V_2O_5 (V_2O_5/porcelain) increases during the first hours of the experimental run. This is evidenced by a monotonous increase in the durene conversion (X_d), which achieves 100% in 8 h at 410°C and V_d = 5000 h^{-1} (Table 1). Then the activity does not change over the test period (1500 h).

A growth of durene conversion is accompanied by an increase in the selectivity to PMDA (S_P) due to the transformation of the products of the partial oxidation of the raw material to PDMA. The maximal value of S_P equal to 42–43 mol % is achieved in 12 h (Fig. 9, curve *1*) and remains constant for the next 5–10 h. Then, the conversion decreases because of the formation of the products of complete oxidation and achieves ~36–38 mol % in 40–44 h of operation. When the oxidation period increases further, S_P does not change.

When this sample is additionally treated thermally at 600°C for 2 h, its initial activity decreases compared

to that of the V_2O_5/porcelain sample calcined at 450°C for 9 h. As a result, the time for achieving 100% conversion and a stationary state of the catalyst increases under the same conditions of oxidation. Note that the maximal S_P is higher and equals 51–56 mol %. However, it decreases to ~38 mol % when the stationary state is achieved (Fig. 9, curve *2*).

When the V^{5+} ions in the V_2O_5/porcelain sample calcined at 450°C for 9 h are reduced to V^{3+} in a hydrogen flow, the catalyst becomes more active but poorly selective to PDMA. Complete durene conversion over this sample is found already 2 h after the onset of the process but S_P is only 10–12 mol % (Fig. 9, curve *3*). Other reaction products consist of carbon oxides and water. With time, S_P increases to the stationary values found for other samples.

Thus, a change in the temperature of preliminary calcination and treatment in the oxidative medium result in the V_2O_5/porcelain samples, which essentially differ in their initial catalytic behavior. However, this difference disappears in several tens of hours of durene oxidation under conditions close to industrial ones. The stationary state of the catalyst is achieved in which S_P is lower than the maximal S_P found under the conditions used in this work.

The above findings indicate that the lower S_P value for the V_2O_5/porcelain catalyst in the stationary state is due to its deep reduction. The question arises as to why the reduction of V^{5+} to V^{4+} and V^{3+} decreases S_P. We have found [30] that the reduction of V_2O_5 leads to an increase in the concentration of adsorption sites for a hydrocarbon capable of forming strongly adsorbed hydrocarbon complexes, which are not desorbed from the catalyst surface in the absence of oxygen in the gas phase even at 400°C. When oxygen is fed, these complexes interact with oxygen and transform into carbon oxides and water probably through carbonate-carboxylate structures or carbonyl and peroxide compounds [29]. This suggests the participation of both gas-phase oxygen and weakly bound oxygen of the catalyst lattice.

The catalytic behavior of the V–Ti systems with C_V greater than 30 wt % do not differ from that of the V_2O_5/porcelain catalyst. TiO_2 does not catalyze durene oxidation under the conditions studied. The V–Ti systems with C_V from 1 to 30 wt % are more active than the V_2O_5/porcelain samples, and durene is completely converted under milder conditions. The minimal T_r for the VT20 sample at which X_d = 100% is lower by 50°C than that for the V_2O_5/porcelain sample at the same contact times. The higher activity of the V–Ti systems is due to the formation of the surface vanadia–titania compounds [25].

The activation of these systems differs from that for the V_2O_5/porcelain described above. Under the experimental conditions, X_d = 100% is achieved in the first hours of the experiment and S_P increases during 5–10 h (Fig. 10) with a simultaneous decrease in the yield of the products of complete durene oxidation. On the sample containing only V_2O_5, S_P passes through a maximum when the catalyst reaches the stationary state (Fig. 9), which is due to V_2O_5 deep reduction. This is accompanied by the appearance of the sites for complete durene oxidation. The absence of a similar maximum in the case of the V–Ti systems with C_V from 1 to 30 wt % is explained by the fact that the degree of reduction of these systems by the reaction medium is lower because of the higher rates of reoxidation of V^{3+} ions, which at least partially enter the highly dispersed surface structures. In addition, the high surface area of the active component in the V–Ti systems (Fig. 4) determines a lower "durene load" per surface unit and consequently a lower degree of V^{5+} reduction. An increase in S_P during the initial hours of durene oxidation is due to the removal of weakly bound oxygen, responsible for complete oxidation, from the catalyst.

The selectivity of the V–Ti systems that achieved the stationary state is primarily determined by the catalyst composition. The selectivity increases to 58–60 mol % with increasing C_V from 1 to 20 wt % (Fig. 11). With a further increase in C_V to 30 wt %, S_P does not change and then gradually decreases to the value characteristic of the V_2O_5/porcelain sample.

Both the higher activity of a series of vanadia–titania catalysts and their higher S_P compared with V_2O_5 are likely due to the fact that the surface vanadia–titania compounds (sites I and II) are formed upon the deposition of V_2O_5 onto the TiO_2 (anatase) surface and the concentration of these sites depends on C_V. As was mentioned above, sites I are formed at low C_V (samples VT1 and VT3). At higher C_V (samples VT3, VT5, etc.), sites II appear. According to [22, 25], sites I are respon-

Table 1. Durene conversion on the V_2O_5/porcelain catalyst with time (T_r = 410°C, C_d = 0.14 vol %, V_d = 5000 h^{-1})

Characteristics of sample	Conversion, mol %			
	time, h			
	2	4	8	12
Calcined in air at 450°C for 4 h	71.1	92.2	100	100
Calcined additionally at 600°C for 2 h	60.8	72.6	91.5	100
Reduced in a H_2 flow at 450°C for 2 h	100	100	100	100

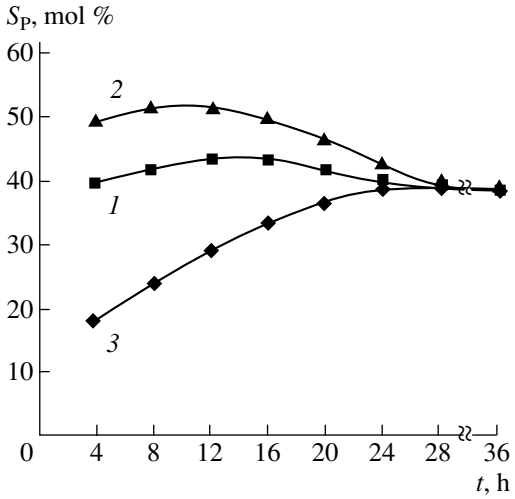

Fig. 9. A plot of S_P in durene oxidation over the V_2O_5/porcelain catalyst vs. time (T_r = 410°C, C_d = 0.14 vol %, V = 5000 h^{-1}): (*1*) sample was calcined in air at 450°C for 9 h; (*2*) sample is additionally calcined at 600°C for 2 h; and (*3*) sample is reduced in a H_2 flow at 450°C.

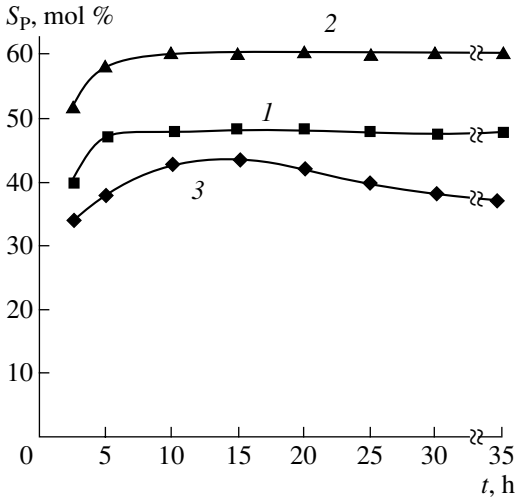

Fig. 10. Plot of S_P in durene oxidation over the V–Ti catalysts of VT*m* series vs. time (T_r = 410°C, C_d = 0.14 vol %, V = 5000 h^{-1}, X_d = 100%): (*1*) VT5, (*2*) VT20, and (*3*) VT40, VT60.

sible for complete *o*-xylene oxidation and sites II are responsible for its oxidation to phthalic anhydride. Taking into account the structural similarity of durene and *o*-xylene molecules, one can suggest that durene is also oxidized to carbon oxides and water on sites I and to PMDA on sites II. Durene molecules are adsorbed on sites II through the activation of the CH_3 groups with the participation of the OH groups bound with V^{5+}, and this is accompanied by the reduction of V^{5+} to V^{3+}. The active sites are rapidly reoxidized with oxygen of the gas phase, and the products of partial durene oxidation and water are simultaneously desorbed. The participation of V_2O_5 mobile oxygen in the reoxidation of the surface site is also possible. The V_2O_5 phase is formed simultaneously with sites I and II and barely affects the activity and selectivity of the V–Ti catalytic systems. The ratio between sites I and sites II changes with C_V in favor of sites II, and this is likely the reason for the S_P increase. With a further increase in C_V, S_P does not change in some range of C_V and then decreases because of blocking the V–Ti compounds by large V_2O_5 crystallites. As a result, a maximum appears on the curve describing S_P as a function of C_V. Note that after reaching the stationary state of the VT20 and VTG samples, their activities become close, and the maximal selectivities S_P become 58–60 and 65–57%, respectively.

At a constant composition of the catalyst, S_P depends on the conditions of durene oxidation. This is 54.6 mol % for the VT20 sample at 390°C and a space velocity of 7000 h^{-1}. With increasing temperature to 410°C, S_P increases to 59.0 mol %. A further increase in temperature results in a decrease in S_P. This character of S_P variation with temperature is found for all samples and is explained by the fact that the rates of the stages of the conversion of intermediates to PMDA increase with increasing temperature. PMDA is resistant to oxidation to CO_2 at temperatures up to 430°C. At higher temperatures, the oxidation rate of PMDA to CO_2 increases and S_P decreases.

Note that the thermal treatment of the of VT*m* and VTG samples in air at 600°C for 2 h results in their irreversible deactivation because of sintering of the surface structures and the partial interaction of vanadium cations with TiO_2 to form solid solutions [12].

Whereas the activities and S_P for the VT20 and VTG samples in durene oxidation are close after the stationary state is reached, their stabilities differ significantly. The catalytic behavior of the VTG samples in durene oxidation does not change even in 3800 h (Table 2).

The stability of the VT*m* samples is markedly lower. After 400 h of operation, S_P on the VT10 catalyst is 43–45 mol % at the complete durene conversion (Table 2). This S_P is close to the maximal value found for VT10. However, after 1150 h, it decreases to 28–30 mol % because of the enhancement of the complete durene oxidation; that is, the catalyst deactivates. Note that an attempt to reactivate the catalyst by treatment in air at 450–500°C failed.

An increase in the V_2O_5 concentration to 20 wt % at the same preparation procedure (VT20) did not improve the catalyst stability, although the PMDA yield in durene oxidation was 58–60 mol % in 400 h. As was mentioned, a further increase in the V_2O_5 content to 60 wt % results in the catalyst close to V_2O_5 in properties. The catalyst is stable but less active and selective than the optimal vanadia–titania samples.

Thus, when vanadia–titania catalysts are prepared using well crystallized TiO_2 (anatase) with low concentration of the surface OH groups and rutile additives,

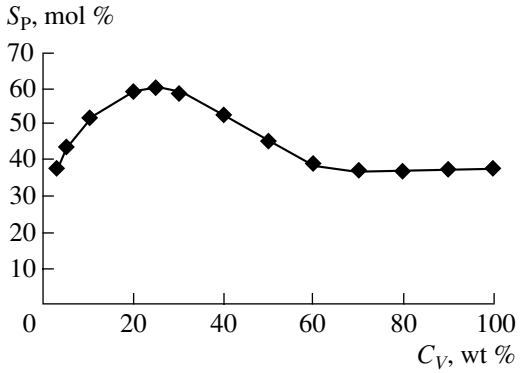

Fig. 11. Plot of S_P in durene oxidation over the V–Ti catalysts of BT*m* series vs. V_2O_5 content. T_r = 410°C, C_d = 0.14 vol %, V = 5000 h^{-1}, X_d = 100%.

the formation of active vanadia–titania compounds is hampered and their concentration is small. Vanadium is present mostly in the form of V_2O_5 crystallites and V_2O_5 solid solutions in rutile. These catalysts are unstable during prolonged durene oxidation.

When a mixture of TiO_2 (anatase) and hydrated highly dispersed $TiO_2 \cdot nH_2O$ is used as a support, the vanadium and OH groups interact on the surface to form surface V–Ti compounds, which determine the catalytic behavior of the sample. Under these conditions, the catalyst is stable over a long period of performance.

TO conclude, let us discuss the role of excess (relatively to a monolayer of V–Ti compound) V_2O_5 in the vanadia–titania catalysts. Comparison of their catalytic properties with those of V_2O_5/porcelain in durene oxidation allows us to conclude that the presence of crystalline V_2O_5 in these catalysts does not affect substantially their activity and S_P. Nevertheless, it is well known that practically all industrial catalysts contain a substantial amount of excess V_2O_5 (from 5.0 to 25.0 wt %), although ~3 wt % V_2O_5 is sufficient for the monolayer coverage of the surface with $S_{sp} \approx 30$ m^2/g. This can be associated with the fact that excess vanadia is needed to form a monolayer in industrial catalysts because of the nonuniformity of coverage caused by the preparation procedure. However, we cannot rule out that the presence of V_2O_5 in the surface structures can improve the stability of their operation due to mobile oxygen, which is retained at the high degree of oxidation of vanadium cations in the surface V–Ti compounds.

Table 2. Catalytic properties of various samples vs. time of durene oxidation (C_d = 0.14 vol %, V_d = 9000 h^{-1})

Sample	Temperature of complete conversion, °C	S_P, mol %
After 400 h oxidation		
VT10	390	43–45
VT20	390	65–67
VT60	430	40–41
VTG	390	65–67
After 1150 h oxidation		
VT10	430	28–30
VT20	430	28–30
VT60	430	40–41
VTG	390	65–67
After 3800 h oxidation		
VT60	430	40–41
VTG	390	65–67

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