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Effect of the Mechanochemical Treatment of a V_2O_5/MoO_3 Oxide Mixture on Its Properties

V. A. Zazhigalov[a], **S. V. Khalameida**[a], **N. S. Litvin**[a], **I. V. Bacherikova**[a], **J. Stoch**[b], **and L. Depero**[c]
[a] *Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Kiev, Ukraine*
e-mail: zazhigal@ispe.kiev.ua
[b] *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland*
[c] *University of Brescia, Brescia, Italy*

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Abstract—The mechanochemical treatment of a V_2O_5/MoO_3 oxide mixture (V/Mo = 70/30 at %) was performed in planetary and vibratory mills under varying treatment times and media. The resulting samples were characterized using XRD analysis, micro-Raman spectroscopy, and XPS; their specific surface areas and catalytic activities in *n*-butane and benzene oxidation reactions were determined. It was found that the treatment of the oxide mixture in water resulted in chaotic degradation of the parent oxides, a decrease in crystallite sizes, and an increase in the specific surface area at a sufficiently uniform oxide distribution over the sample. The treatment in ethanol was accompanied by an anisotropic deformation of the V_2O_5 crystal by layer sliding in parallel to the vanadyl plane (010) and a chaotic degradation of MoO_3 crystals. This process was accompanied by the partial nonuniform supporting of vanadium oxide crystals onto the surface of molybdenum oxide to increase the V/Mo ratio on the sample surface. In this case, the particle size of oxides decreased and the specific surface areas of samples increased. It was found that the treatment of the oxide mixture in air (dry treatment) resulted in the most significant decrease in the sizes of V_2O_5 and MoO_3 crystals and a growth in the specific surface area. The amorphization of the parent oxides and the formation of MoV_2O_8 were observed as the treatment time was increased; in this case, an excess of amorphous vanadium oxide was supported onto the surface of this compound. It was found that, in all types of mechanochemical treatment, the binding energies of the core electrons of vanadium and molybdenum remained almost unchanged to indicate the constancy of the oxidation states of these elements. Mechanochemical treatment resulted in an increase in the activity of the samples in *n*-butane and benzene oxidation reactions and in an increase in the selectivity of maleic anhydride formation. In this case, an increase in the specific catalytic activity of the samples correlated with a decrease in the crystallite size of vanadium oxide, whereas selectivity correlated with an increase in the relative concentration of the V_2O_5 plane (010). In these reactions, samples after dry treatment exhibited a maximum activity, which can be related to the formation of MoV_2O_8.

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INTRODUCTION

Prospects for the use of mechanochemistry to activate solids have been described adequately in the scientific literature (e.g., [1–7]). Catalysis is an area of application of mechanochemistry, which is used for the modification of the properties of well-known catalysts and for the synthesis of new catalytic systems (e.g., see [8–16]). At the same time, we note that systematic studies in this area remain insufficient, and data on the effect of treatment conditions on the physicochemical and catalytic properties of substances should be accumulated for the target-oriented use of mechanochemistry in catalysis.

It is well known that many catalysts for the partial oxidation of hydrocarbons contain vanadium and molybdenum oxides and a complex V–Mo–O composition is used in the oxidation of benzene, propylene, and acrolein and the oxidative ammonolysis of propane among other things [17–23]. The use of mechanochemical treatment for modifying the properties of individual vanadium and molybdenum oxides has been considered in a number of publications [24–34]. In this case, it was found that both chaotic degradation of oxide crystals and anisotropic shear deformation can occur depending on treatment conditions. The effects of loading and the treatment medium on the specific surface area and morphology of oxides were found. Mechanochemical treatment resulted in the reduction of metal ions initially on the surface and then in the bulk oxide and in the appearance of new phases. It was found that changes that occurred in oxides under mechanochemical treatment significantly affected their catalytic properties to increase activity and selectivity in the oxidation reactions of various hydrocarbons, for example, *n*-butane, propane, and benzene.

Data on the activation of simple oxides indicated that the mechanochemical synthesis of complex V–Mo oxide catalysts is promising. There are a few publica-

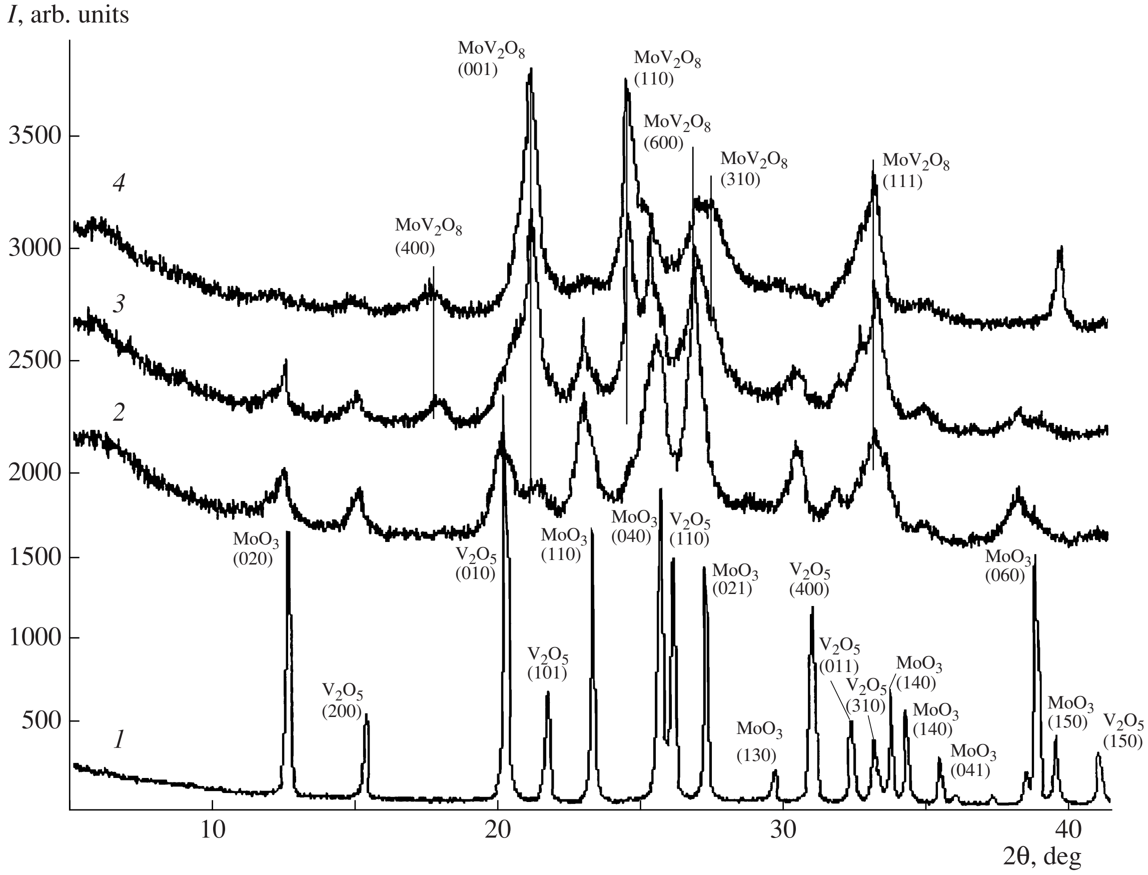

Fig. 1. X-ray diffraction patterns of samples after mechanochemical treatment in air for (*2*) 10, (*3*) 20, or (*4*) 40 min and (*1*) the initial oxide mixture.

tions on the synthesis of V–Mo–O samples by mechanochemical treatment [11, 35, 36]. These publications report on studies of the physicochemical properties of this system using various techniques (XRD analysis and EPR, NMR, and IR spectroscopy); however, the catalytic properties of the samples were not determined. Note that a composition with an excess of molybdenum oxide (V/Mo < 0.5) was studied previously [11, 35, 36]. At the same time, it is well known [17, 18, 21–23] that systems containing 30 at % MoO_3 and 70 at % V_2O_5 are more effective in hydrocarbon oxidation processes; a solid solution of molybdenum oxide in vanadium pentoxide is formed in these systems. In this context, in this work, we consider the effect of the mechanochemical treatment of an oxide mixture with the specified composition in various apparatuses and media on the physicochemical and catalytic properties of this mixture.

EXPERIMENTAL

A mixture of vanadium and molybdenum oxides (analytical grade) with the ratio V/Mo = 70 : 30 at % was used for mechanochemical treatment. The oxide mixture was treated (a) in a high-energy planetary mill P1 (cylinder speed of 3000 rpm; metal balls, d = 10 mm; ball weight of 450 g; oxide mixture weight of 20 g; treatment time of 10–40 min) and (b) in a Fritsch Pilverisette-1 vibratory mill V1 (agate balls 12 mm in diameter; ball weight of 180 g; oxide weight of 20 g; treatment time of 60–240 min; vibration frequency of 50 Hz). Water and ethanol were used as treatment media; dry treatment in air was also performed.

The specific surface areas of samples were measured by the thermal desorption of argon on a Gazokhrom-1 instrument. The phase composition of the samples was studied by powder diffraction on a Philips MPD 1880 diffractometer (monochromated CuK_α radiation). The relative intensities of reflections and the widths at half height were determined using the APD software (Philips, version 3). The micro-Raman spectra were measured on a Dilor Labram spectrograph (HeNe laser, 632.8 nm). The oxidation states of the elements and the surface compositions of the samples were determined by XPS on a VG ESCA-3 instrument (AlK_α radiation; monochromator; C 1*s* reference line, 284.8 eV). The processing and analysis of the spectra was performed as described previously [37].

The catalytic activity of the samples in hydrocarbon oxidation reactions was studied in a flow-type system

Table 1. Effect of mechanochemical treatment conditions on the properties of the V_2O_5–MoO_3 sample

Treatment conditions		SSA, m^2/g	XRD data				
medium	time, min		$I_{110}V_2O_5/I_{010}V_2O_5$	$I_{020}MoO_3/I_{010}V_2O_5$	$I_{060}MoO_3/I_{010}V_2O_5$	$D^*_{V_2O_5}$, nm	$D^*_{MoO_3}$, nm
–	–	3.1	63/100	76/100	60/100	67	72
Water, P1	10	8.2	62/100	70/100	62/100	60	70
Water, P1	20	10.0	64/100	69/100	56/100	54	64
Water, P1	30	13.4	60/100	75/100	55/100	47	61
Water, P1	40	12.8	62/100	70/100	54/100	40	53
Water, V1	60	4.2	64/100	76/100	63/100	59	68
Water, V1	120	4.4	63/100	75/100	60/100	54	67
Water, V1	240	4.9	62/100	76/100	63/100	50	65
Ethanol, P1	10	5.3	56/100	69/100	56/100	61	68
Ethanol, P1	20	6.7	48/100	62/100	56/100	54	57
Ethanol, P1	30	7.4	28/100	64/100	58/100	45	48
Ethanol, P1	40	10.0	22/100	60/100	58/100	37	39
Ethanol, V1	60	3.4	63/100	69/100	57/100	61	70
Ethanol, V1	120	3.5	56/100	68/100	57/100	56	62
Ethanol, V1	240	3.6	58/100	71/100	55/100	49	56
Dry, P1	10	12.7	0/100	67/100	60/100	21**	26
Dry, P1	20	13.4	–	–	–	14**	15
Dry, P1	30	15.0	–	–	–	13***	
Dry, P1	40	18.2	–	–	–	19***	

* The particle size calculated from the Scherrer equation for the (110) planes of V_2O_5 and MoO_3.

** Calculated for the (200) plane of V_2O_5.

*** Calculated for the (001) plane of MoV_2O_8.

with a quartz reactor 8 mm in diameter and 60 cm in length. The reactor was loaded by alternating a layer (1 cm) of the catalyst (particle size of 0.25–0.50 mm) and a layer (1 cm) of an inert material (crushed quartz). The amount of the catalyst loaded was 4 cm^3. The oxidation of *n*-butane (1.7 vol % in air) was performed over a temperature range of 350–550°C varying the contact time within the range of 0.6–2.4 s. The oxidation of benzene (1 vol % in air) was studied at 300–550°C and contact times of 0.5–2.0 s. The online analysis of the initial components and reaction products was performed by chromatography as described elsewhere [38].

RESULTS AND DISCUSSION

The diffraction pattern of a sample of the initial oxide mixture is a superposition of peaks due to V_2O_5 and MoO_3 phases (Fig. 1; Table 1 summarizes the ratios between main oxide line intensities). The mechanochemical treatment of the oxide mixture in water did not change the peak positions in the X-ray diffraction pattern, which are independent of the type of the mill and the treatment time. As can be seen in Table 1, the relative intensity of oxide reflections also changed only slightly as a result of this treatment. At the same time, a line broadening was observed, and the average particle sizes of V_2O_5 and MoO_3 decreased with treatment time

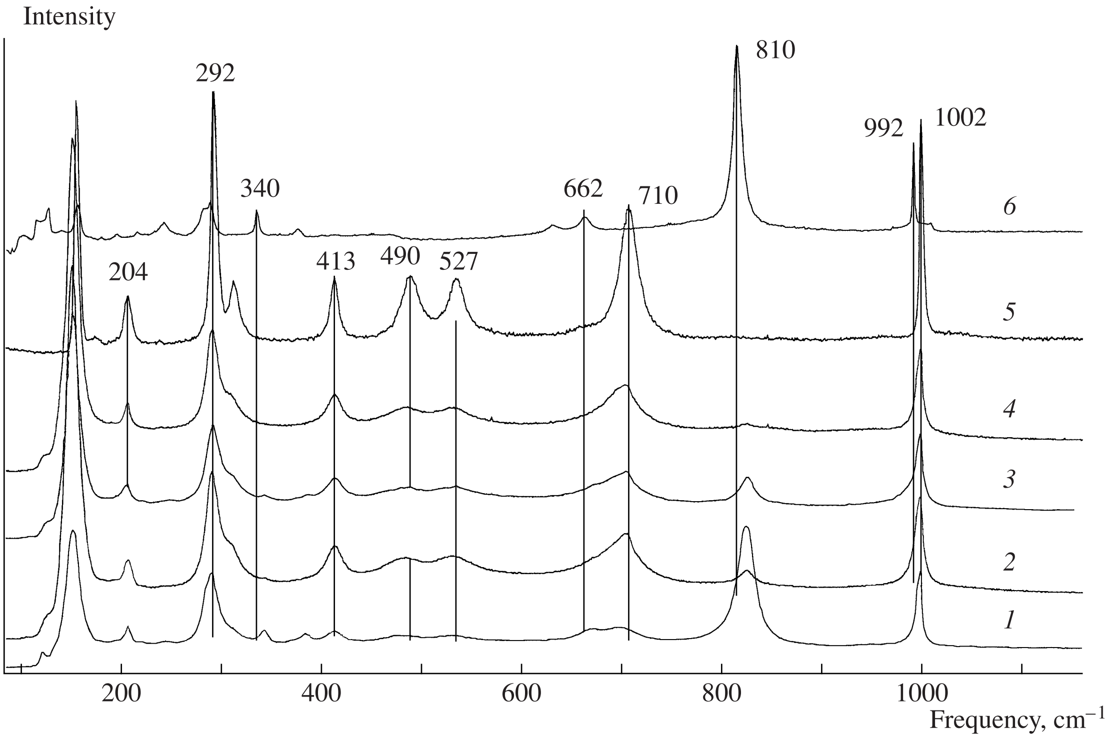

Fig. 2. Micro-Raman spectra of an oxide mixture after mechanochemical treatment in ethanol for (*1*) 10, (*2*) 20, (*3*) 30, or (*4*) 40 min. Initial oxides: (*5*) V_2O_5 and (*6*) MoO_3.

in both types of apparantus, as found by calculations using the Scherrer equation (Table 1). The specific surface area (*S*) of the sample simultaneously increased. Maximum changes in the particle size (*D*) and specific surface area were observed upon treatment in a planetary mill, and they were reached in mill P1 in a shorter time than in mill V1. Thus, the orders of change in the specific surface area and particle size $S(\mathrm{P1}) > S(\mathrm{V1})$ and $D(\mathrm{P1}) < D(\mathrm{V1})$ are consistent with energies transferred to solids on treatment in the specified apparatuses: $E(\mathrm{P1}) > E(\mathrm{V1})$. The experimental results allowed us to assume that, in the mechanochemical treatment of a mixture of vanadium and molybdenum oxides in water, oxide crystals underwent chaotic degradation that led to a decrease in crystal sizes and an increase in the specific surface area.

Analogously to the above treatment, the mechanochemical treatment of a mixture of V_2O_5 and MoO_3 in ethanol did not change qualitatively the peak positions in the X-ray diffraction patterns but caused changes in reflection intensities (Table 1). The relative intensity of the V_2O_5 (110) reflection decreased considerably, and the intensity of the MoO_3 (020) reflection decreased to a lesser extent, whereas the intensity of the MoO_3 (060) reflection remained almost unchanged and decreased only slightly. In this case, the specific surface areas of the samples increased to a somewhat lesser extent than upon treatment in water. On the contrary, the oxide particle sizes decreased. As in the previous case, these changes were minimal upon treatment in a vibratory mill. Based on the experimental results, we can hypothesize that an anisotropic deformation of the V_2O_5 crystal by layer sliding in parallel to the vanadyl plane (010) occurred upon treatment in ethanol. An analogous phenomenon was also observed in the treatment of individual V_2O_5 in ethanol [29, 30]. At the same time, a decrease in the intensity of reflections due to molybdenum oxide suggests its chaotic degradation, which is also analogous to the effect observed on the treatment of MoO_3 [32].

Thus, XRD data indicate that the mechanochemical treatment of a mixture of V_2O_5 and MoO_3 in water and ethanol did not cause the formation of new phase compounds; however, changes in the structures of the parent oxides occurred in this case, and these changes depended on the treatment medium and time.

Figure 2 shows the micro-Raman spectra; these spectra indicate that the absorption bands characteristic of vanadium oxide remained almost unchanged upon the treatment of an oxide mixture of V_2O_5 and MoO_3 in ethanol. At the same time, a shift in the absorption bands of MoO_3 was observed after treatment for 10 min: absorption bands at 810, 662, and 340 cm^{-1} shifted to 821, 667, and 348 cm^{-1}, respectively. The intensities of all absorption bands characteristic of MoO_3 considerably decreased with treatment time, and their intensities became insignificant after treatment in ethanol for 40 min. Another behavior was observed in a sample upon treatment in water. Data given in Fig. 3

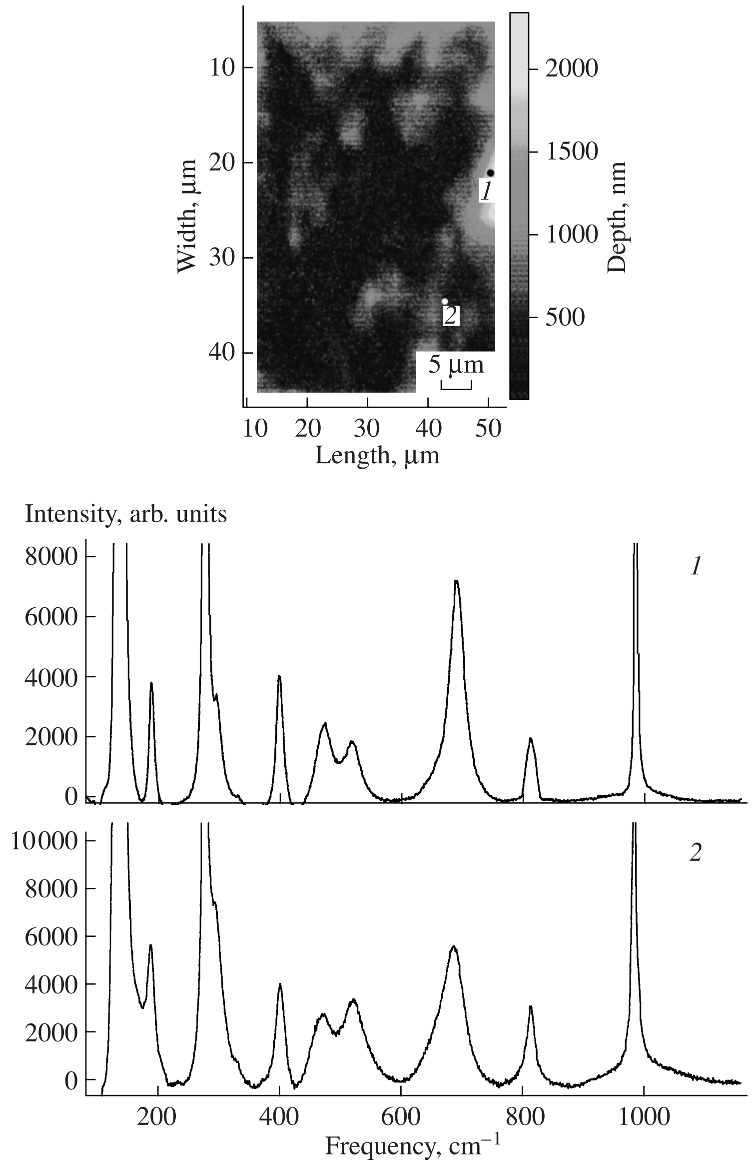

Fig. 3. Micro-Raman spectra for points *1* and *2* in a fragment of the sample surface after mechanochemical treatment in water for 40 min.

indicate that, even after a 40-min treatment of the oxide mixture in water, the spectra obtained at two points (*1* and *2*) in a sample fragment (the size of an analyzed zone was ~2 μm at either of the points; the depth of analysis was to 2 μm) exhibited an intense absorption band at 810 cm^{-1}, which almost disappeared upon treatment in ethanol. As can be seen, the spectra obtained at the two sites of the surface fragment exhibited all of the other absorption bands characteristic of vanadium and molybdenum oxides. The intensities of absorption bands at different points (Fig. 3, points 1 and 2) of the test surface fragment of the sample after treatment in water differed only slightly; this fact suggests a uniform distribution of oxide particles.

Thus, the experimental results indicate that, although the processes of mechanochemical treatment of a mixture of vanadium and molybdenum oxides in water and ethanol exhibited a number of common features, the observed changes in the oxide system were different. Chaotic degradation of crystals occurred during treatment in water to result in a decrease in the crystal size and a uniform distribution of particles. The treatment in ethanol led to an anisotropic deformation of vanadium oxide parallel to the (010) plane and a chaotic degradation of molybdenum oxide. In this case, the supporting (smearing) of vanadium oxide on molybdenum oxide and the surface coverage of the latter with V_2O_5 took place; this was reflected in a decreased intensity of the absorption band at 810 cm^{-1} (Fig. 2) in micro-Raman spectra. The surface coverage with vana-

Table 2. XPS characterization of the V_2O_5–MoO_3 sample after mechanochemical treatment

Treatment conditions		XPS data				
medium	time, min	Electron binding energies, eV			V/Mo ratio	Calculated value of *n**
		V2*p*3/2	Mo3*d*5/2	O1*s*		
–	–	517.6	232.9	531.0	3.06	4.71
Water, P1	10	517.5	233.0	530.7	3.34	4.84
Water, P1	20	517.8	233.1	530.9	3.41	4.91
Water, P1	30	517.7	233.0	531.0	3.38	4.78
Water, P1	40	517.8	233.0	530.9	3.35	4.91
Water, V1	60	517.7	233.0	530.9	3.36	4.84
Water, V1	120	517.9	233.2	531.0	3.24	4.91
Water, V1	240	517.7	233.0	531.0	3.30	4.78
Ethanol, P1	10	517.7	233.0	531.0	3.56	4.78
Ethanol, P1	20	517.6	232.9	530.9	4.03	4.78
Ethanol, P1	30	517.9	233.2	531.1	4.32	4.84
Ethanol, P1	40	517.8	232.9	530.9	4.48	4.91
Ethanol, V1	60	517.7	233.0	531.0	3.57	4.78
Ethanol, V1	120	518.0	233.3	531.2	3.62	4.71
Ethanol, V1	240	517.9	233.1	530.9	3.95	4.97
Dry, P1	10	517.7	232.9	530.8	5.55	4.91
Dry, P1	20	518.0	233.1	531.4	5.61	4.71
Dry, P1	30	517.7	233.0	531.1	4.62	4.71
Dry, P1	40	517.8	232.9	530.9	4.67	4.91

* The oxidation state of vanadium (V^{n+}) derived from XPS data using an equation from [39].

dium oxide was also supported by XPS data (Table 2). As can be seen, unlike the treatment in the presence of water, the treatment in ethanol resulted in an increase in the V/Mo ratio in the surface layer. Micro-Raman spectroscopic data (Fig. 4) also suggest that this supporting of vanadium oxide is an irregular process. As can be seen, the spectra at points *1* and *2* in a surface fragment were considerably different. At point *2*, all of the absorption bands characteristic of molybdenum oxide (along with the absorption bands of vanadium oxide) were observed, whereas the absorption band at 810 cm^{-1} almost disappeared at point *1*. At the same time, the binding energies of V $2p_{3/2}$ and Mg $3d_{5/2}$ electrons in the XPS spectra (Table 2) remained almost constant upon treatment in both ethanol and water; this fact suggests that the oxidation states of these elements remained unchanged upon mechanochemical treatment. Table 2, which summarizes the oxidation states of vanadium calculated from XPS spectra using an equation proposed by Coulston et al. [39], demonstrates the constancy of this oxidation state. The underestimated values of the calculated oxidation state of vanadium can be explained by the fact that the equation proposed by Coulston et al. [39] was defined for individual vanadium oxides. In the presence of a few types of atoms (V and Mo in our case), the capability of the oxygen atom to withdraw electron density from them should be taken into account and the so-called group shift [40–42] should be determined by the summation of Madelung energies over all types of atoms.

Another behavior was observed in the dry treatment of the V_2O_5/MoO_3 mixture. As can be seen in Fig. 1, a dramatic broadening of reflections characteristic of vanadium and molybdenum oxides and the appearance

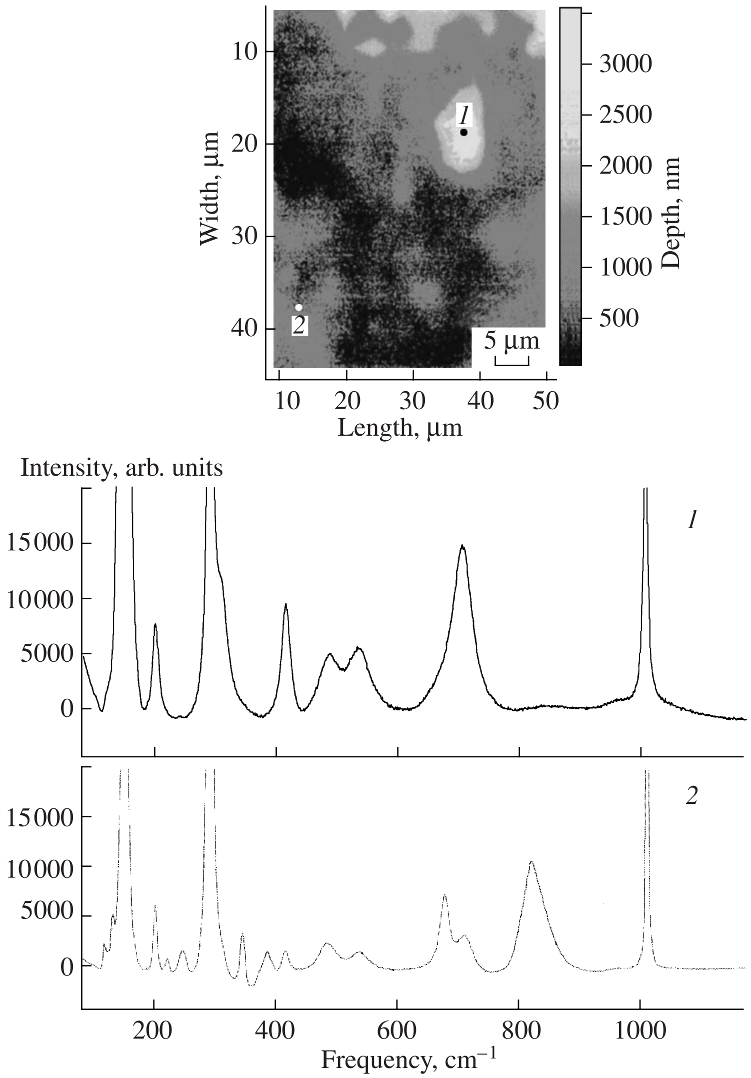

Fig. 4. Micro-Raman spectra for points *1* and *2* in a fragment of the sample surface after mechanochemical treatment in ethanol for 40 min.

of new lines in the diffraction pattern were observed even after treatment for 10 min. As the time of mechanochemical treatment was increased, the intensity of these new reflections, which characterized the formation of a MoV_2O_8 phase (JCPDS 18-851), increased and the reflections of the parent oxides almost disappeared from the spectrum. The specific surface area of the sample increased with treatment time (Table 1), whereas the particle sizes of the parent oxides dramatically decreased even after a 10-min treatment. In this case, the specific surface area reached a maximum value, as compared with treatment in other media, whereas the particle sizes of the parent oxides reached minimum values. On the contrary, the particle size of the resulting MoV_2O_8 phase increased in the course of treatment.

Figure 5 shows the micro-Raman spectra at different sites (points *1* and *2*) of a fragment of the sample surface after dry treatment for 40 min. These spectra exhibited almost equal absorption band intensities; that is, a uniform distribution of the components was observed. At the same time, we note that the absorption band that characterizes the M=O bond shifted to 980 cm^{-1} and the absorption bands due to M–O–M' bridging bonds shifted to 850 and 690 cm^{-1}. These changes in the Raman spectrum can be due to the formation of a new compound, MoV_2O_8. The XPS data given in Table 2 suggest that the oxidation states of vanadium and molybdenum remained unchanged in the course of dry treatment. These data indicate that the binding energies of electrons of these elements, as well as the calculated oxidation states of vanadium, remained constant. On the other hand, the dry mechanochemical treatment of a mixture of vanadium and molybdenum oxides resulted in a dramatic increase in the V/Mo ratio on the surface, as follows from XPS data

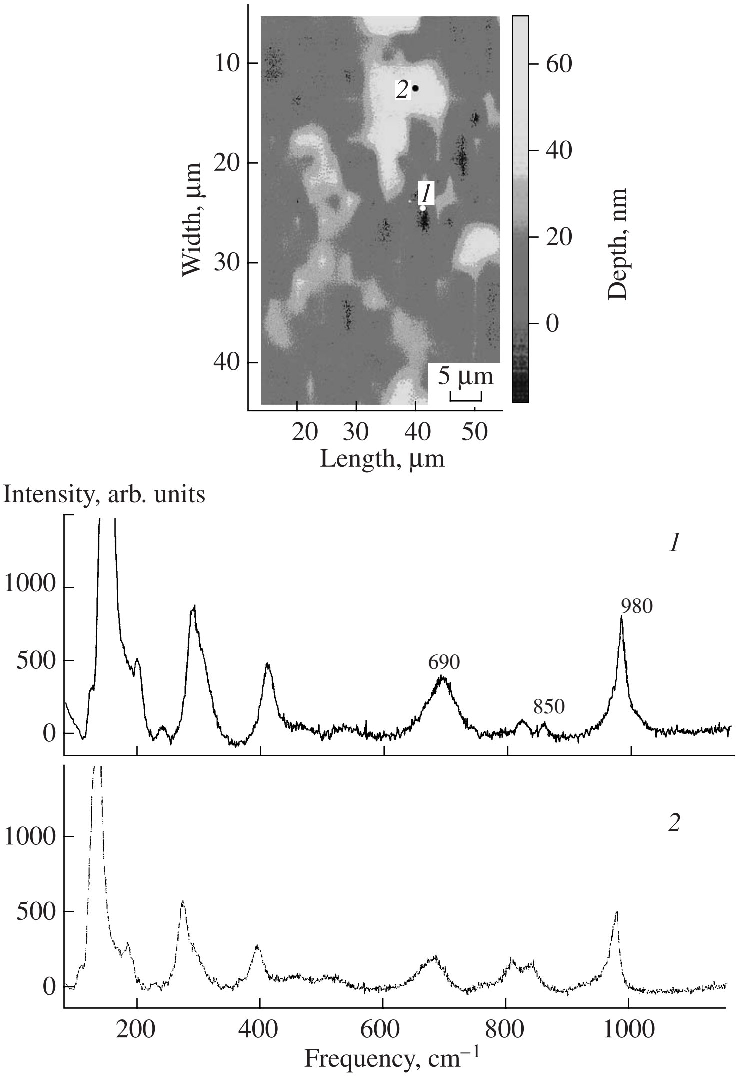

Fig. 5. Micro-Raman spectra for points *1* and *2* in a fragment of the sample surface after mechanochemical treatment in air for 40 min.

(Table 2). The set of the above data suggests, along with the formation of the new compound MoV_2O_8, the amorphization of an excess of V_2O_5 (the absence of reflections in x-ray diffraction patterns), which covers the surface of this compound.

A study of the reaction of *n*-butane oxidation demonstrated that maleic anhydride and carbon oxides were the main products of this reaction in the presence of the initial oxide mixture sample and samples after mechanochemical treatment. We found that the activity of the initial oxide mixture in this process was low. However, mechanochemical treatment resulted in a considerable increase in both hydrocarbon conversion and the specific rate of paraffin oxidation. In the course of treatment in the presence of a dispersing agent, the specific rate of the process increased from 2.7 (in the initial sample) to 9.5×10^{-4} mol h^{-1} m^{-2}. A comparison between the catalytic activity and properties of samples after mechanochemical treatment demonstrated that, regardless of the energy load and the nature of the dispersing agent, a good correlation between the decrease in the particle size of vanadium oxide and the increase in the specific rate of *n*-butane oxidation was observed (Fig. 6, straight line *1*). Dry treatment caused an even greater increase in the rate of oxidation to 14.1×10^{-4} mol h^{-1} m^{-2} in samples in which weak reflections of V_2O_5 were detected by XRD analysis or to 21.1×10^{-4} mol h^{-1} m^{-2} in samples in which they fully disappeared. In the latter case, the particle size of the MoV_2O_8 phase was used as a correlation parameter. The samples after mechanochemical treatment in air exhibited a maximum paraffin conversion of 68–70% at 440°C. The selectivity of maleic anhydride formation in *n*-butane oxidation also increased as a result of the mechanochemical treatment of samples in the presence of a dispersing agent from 4.9% in the initial sample to 20.2% in the sample after

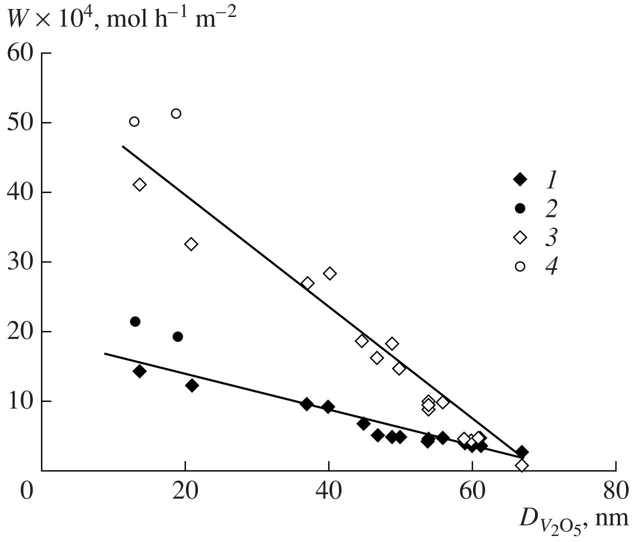

Fig. 6. Dependence of the specific rates of oxidation of (*1*, *2*) *n*-butane and (*3*, *4*) benzene on the crystallite sizes of (*1*, *3*) vanadium oxide and (2, *4*) MoV_2O_8 for the samples of the V_2O_5–MoO_3 mixture after various types of mechanochemical treatment.

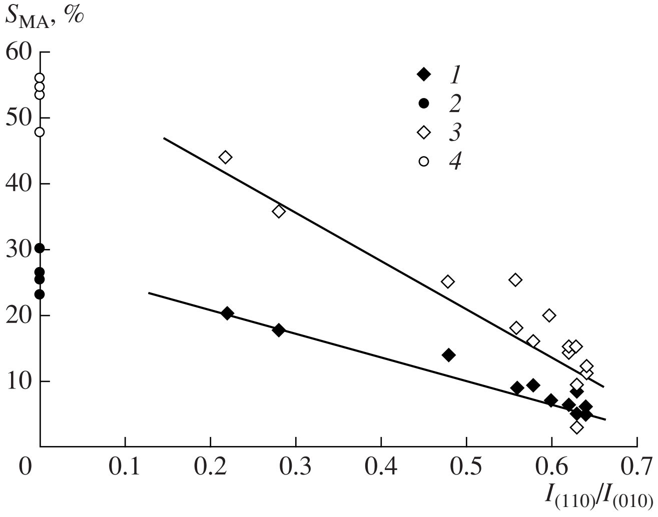

Fig. 7. Dependence of the selectivity of maleic anhydride formation in the oxidation of (*1*, *2*) *n*-butane and (*3*, *4*) benzene on the intensity ratio between the (110) and (010) planes in (*1*, *3*) vanadium oxide for the samples of the V_2O_5–MoO_3 mixture after various types of mechanochemical treatment; (*2*, *4*) samples after dry treatment (P1), which contained no reflections from the (110) plane of V_2O_5 (Table 1).

treatment. In this case, a relationship between the relative concentration of the vanadyl (010) plane in vanadium oxide and the selectivity of maleic anhydride formation was found (Fig. 7, straight line *1*). This selectivity, as well as activity, maximally increased as a result of dry mechanochemical treatment to reach 25–30% (in Fig. 7, points lie in the axis of ordinates because the $I_{(110)}/I_{(010)}$ ratios cannot be determined for these samples).

The oxidation of benzene on the initial mixture of vanadium and molybdenum oxides occurred at a low rate with low selectivity for maleic anhydride (0.8×10^{-4} mol h^{-1} m^{-2} and 3%, respectively). The mechanochemical treatment of the oxide mixture in the presence of a dispersing agent at a minimum treatment time increased the rate of reaction and selectivity for maleic anhydride by factors of 5 and 3, respectively. An increase in the treatment time resulted in a further increase in activity and selectivity. As can be seen in Fig. 6, as in the case of *n*-butane, the specific rate of benzene oxidation increased with decreasing particle size of vanadium oxide. In turn, the selectivity of maleic anhydride formation correlated with changes in the relative concentration of the (010) plane in V_2O_5 (Fig. 7, straight line *2*). As in the case of the *n*-butane oxidation reaction, samples subjected to mechanochemical treatment in air exhibited maximum activity and selectivity in benzene oxidation (see above for the positions of points in Figs. 6 and 7 for these samples). The specific rate of benzene conversion on these samples was higher than the rate of oxidation on the initial oxide mixture by a factor of 50, and a hydrocarbon conversion of 82–85% was reached at 325°C. In this case, the selectivity of maleic anhydride formation was 54–57%.

It is well known that the stable activity of catalysts prepared by mechanochemical treatment presents a problem. We found that an increase in the reaction temperature to 550°C followed by a decrease to an optimum reaction temperature (440 or 330°C in the oxidation of *n*-butane or benzene, respectively) did not change characteristics reached previously at these temperatures.

Thus, the mechanochemical treatment of a mixture of vanadium and molybdenum oxides in various media caused a decrease in the crystallite sizes of the parent oxides. In this case, chaotic degradation of crystals and anisotropic deformation of vanadium oxide accompanied by the supporting of vanadium oxide onto molybdenum oxide occurred in water and ethanol, respectively, whereas dry treatment led to the formation of a new compound (MoV_2O_8) and the supporting of an excess of amorphous vanadium oxide on the surface of this compound. Changes in the structure and morphology of the oxides upon mechanochemical treatment significantly affected the activity and selectivity of the oxides in the catalytic oxidation reactions of different hydrocarbons: a paraffin and an aromatic compound. In this case, regardless of the nature of the hydrocarbon, the activity of catalysts increased with decreasing particle size of vanadium oxide, whereas selectivity increased with exposure of the (010) plane containing vanadyl oxygen in this oxide. Samples subjected to mechanochemical treatment in air exhibited maximum activity and selectivity in both reactions; these samples contained the MoV_2O_8 phase, the presence of which can explain the high performance characteristics of these catalysts.

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