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Chemical and phase transformation in the V_2O_5–$(NH_4)_2Mo_2O_7$ system during the mechanochemical treatment in various media

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Abstract Mechanochemical treatment (MChT) in various media (water, air, ethanol) of the V_2O_5/ammonium dimolybdate composition at the ratio V:Mo = 0.7:0.3 has been carried out. Physicochemical transformations in this system have been studied by means of X-ray powder diffraction (XRD) and thermal analysis as well as FTIR spectroscopy. Ammonium dimolybdate undergoes hydration with formation of 4-aqueous ammonium paramolybdate during the MChT in water. Changes of phase and chemical composition at activation are determined first of all by nature of medium in which milling was carried out. Maximal interaction of components occurs during modification of the studied system in water.

Keywords V_2O_5 · Nonstoichiometric molybdenum oxides · Ammonium dimolybdate · Ammonium paramolybdate · Mechanochemical treatment · Thermogravimetry

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Introduction

Mixed oxide systems formed from vanadium and molybdenum in various proportions of individual components are a basis for hydrocarbons partial oxidation and oxidative dehydrogenation catalysts [1–5]. In particular the mixtures containing 20–30% of molybdenum oxide can be applied as catalysts of selective oxidation of methanol to formaldehyde, benzene to maleic anhydride and other processes. This composition corresponds to one of two fields of catalytic activity for studied system [1, 2]. Activity is associated with the formation of solid solution substitution of vanadium with molybdenum in V_2O_5 [2, 5–8]. The mixed oxides with the above mentioned ratio of components are also used as cathode materials in chemical power sources [9, 10] because they possess maximal electroconductivity [2, 7, 9, 11]. The said solution (α-phase) of the formula $(V_{1-x}Mo_x)_2O_5$ $(0 < x \leq 0.3)$ is usually prepared by calcination in air (up to 650 °C and more) of oxide mixture or their fusion [6, 7, 9, 11, 12].

Another way of α-phase formation consists in evaporation of aqueous solutions of molybdenum and vanadium ammonium salts and following thermal decomposition of the prepared intermediate products [5, 12, 13]. At the time, of heating up to 250 °C causes appearance of ammonium salt of vanadium–molybdenum isopolyacid [12] but up to 400 °C—compounds of variable composition of hexagonal bronzes type $(NH_4)_xV_xMo_{1-x}O_3$ [5, 12]. Compound of the general formula $V_{2-x}Mo_{1+x/2}O_{8-y}$ $(0 \leq x \leq 0.30; y \leq 0.1)$ or β-phase is formed during thermal decomposition of this bronze above 350 °C [5–7, 12].

Xerogels of polyvanadiummolybdenum acid $H_2V_{12-x}Mo_xO_{31+\delta}\cdot nH_2O$ $(0 < x \leq 3,\ -0.3 < \delta \leq 1.3,\ 8.4 \leq n \leq 9.0)$ of similar composition to the above mentioned solid solution were studied in [14, 15]. They were prepared through the decomposition of peroxide solutions of V_2O_5 and molybdenum acid and formation of gels containing large amounts of water. After its removal vanadium–molybdenum oxide (α-phase) is also formed.

Taking into consideration complexity of physicochemical transformations which may occur in the V–Mo–O system it is interesting to apply a non-traditional modern method of synthesis and modification of solids, i.e., a mechanochemical treatment (MChT) [16–19]. It should be noted that mechanochemical synthesis has been already used to prepare multicomponent catalysts based on vanadium and molybdenum, but till now only for the mixtures containing less than 50% vanadium oxide. Moreover, this process has been carried out using only dry treatment, i.e., in air [8, 20]. Mechanochemical activation (MChA) of vanadium oxide and some compounds containing vanadium was studied in detail. The review of obtained results is presented in [17]. The influence of MChT of molybdenum trioxide on its structure is described in [21]. However, so far the results of systematic studies of the effect of MChT conditions in different media on physicochemical properties of mixed vanadium–molybdenum oxides of various compositions have not been published. Therefore, the main aim of this work is to investigate chemical and physicochemical transformations in the system of vanadium pentaoxide–ammonium dimolybdate with a large content of vanadium during its milling in different media. This is one of variants for preparation of V–Mo–O-precursors of catalysts.

Experimental section

Mechanochemical treatment of crystalline V_2O_5 and ammonium dimolybdate (ADM) $(NH_4)_2Mo_2O_7$ (both analytically pure) mixture in the ratio V:Mo = 0.7:0.3 at.% was carried out for 60, 120, 240, and 360 min using a planetary ball mill of Pulverisette-6 type (Fritsch) with a rotation speed of 600 rpm. Ten balls made of silicon nitride with a 15 mm diameter (total ball mass—130 g) were used. The milling media were air ("dry" treatment), ethanol, or water. The $V_2O_5/(NH_4)_2Mo_2O_7$ loading was 10 g. The mass ratio of sample and liquid during the treatment was 0.1.

The starting mixture and products of mechanochemical transformations as well as thermally treated samples were studied by means of X-ray powder diffraction (XRD) using a diffractometer Philips PW 1830 with CuK_α radiation. Rietveld's method was applied for calculation of obtained data. Diffractograms were registered for all samples in identical conditions that allow to compare parameters calculated from them. Curves of thermal and gravimetric analysis were measured on apparatus Derivatograph-C, Paulik, Paulik and Erdey system (MOM, Hungary) in the temperature range 20–600 °C on air, the heating rate—10°/min. The samples weight was equal 35 mg for ADM, 50 mg for V_2O_5/ADM, and 150 mg for individual V_2O_5. It should be noted that thermoanalytical experiments were used for investigation of chemical and phase transformations taking place at MChT of various compounds [18, 22, 23] however were not used for milled V–Mo oxides.

The FTIR spectra in the range 4,000–500 cm^{-1} were registered using spectrometer "Spectrum-One" (Perkin-Elmer). The ratio of sample and KBr in the pellets was 1:20.

Results and discussion

Mechanochemical treatment of ammonium dimolybdate $(NH_4)_2Mo_2O_7$

To simplify the interpretation of the results obtained during grinding of the studied composition, first of all MChA of the initial salt—ammonium dimolybdate was made in various conditions. The initial ADM and the intermediate products of its MChA were investigated by means of comparison of XRD and DT-TG analysis.

Heating on air of the initial salt (ADM) up to 600 °C leads to its decomposition and formation of the rhombohedral form of MoO_3 according to the equation:

$$(NH_4)_2Mo_2O_7 = 2MoO_{3(r)} + 2NH_3 + H_2O \qquad (1)$$

The results of XRD for initial ADM and products of its milling in various media are presented in Fig. 1. XRD patterns indicate that the phase composition does not change and only ADM is present in products of the activation process both in air and ethanol. On the other hand, the intensity of the strongest reflex of ADM decreases as a result of MChA on air (in 3 times) and in ethanol (in 1.5 times). Besides, the TG and DTA curves (Fig. 2) both for initial ADM (ADM_{init}) and that subjected to MChT in air ($ADM–MChT_{air}$) and in ethanol ($ADM–MChT_{eth}$) have the identical form. Thus, three endothermic effects at 205–215, 250, and 325–330 °C are present on the DTA curves. Three stages of mass loss correspond to these effects in all three cases but the total mass loss determined experimentally was 14.2% w/w for the sample ADM_{init}, 13.4% w/w for $ADM–MChT_{air}$ and 14.0% w/w for $ADM–MChT_{eth}$. For the initial sample and samples milled in air and ethanol the first two stages of decomposition (in the temperature range 180–260 °C) proceed with formation of the mixture of the phases of $3MoO_3 \cdot 2NH_3 \cdot H_2O$ composition (ASTM N 20-755) and hexagonal molybdenum trioxide (confirmed by the XRD) according to the scheme:

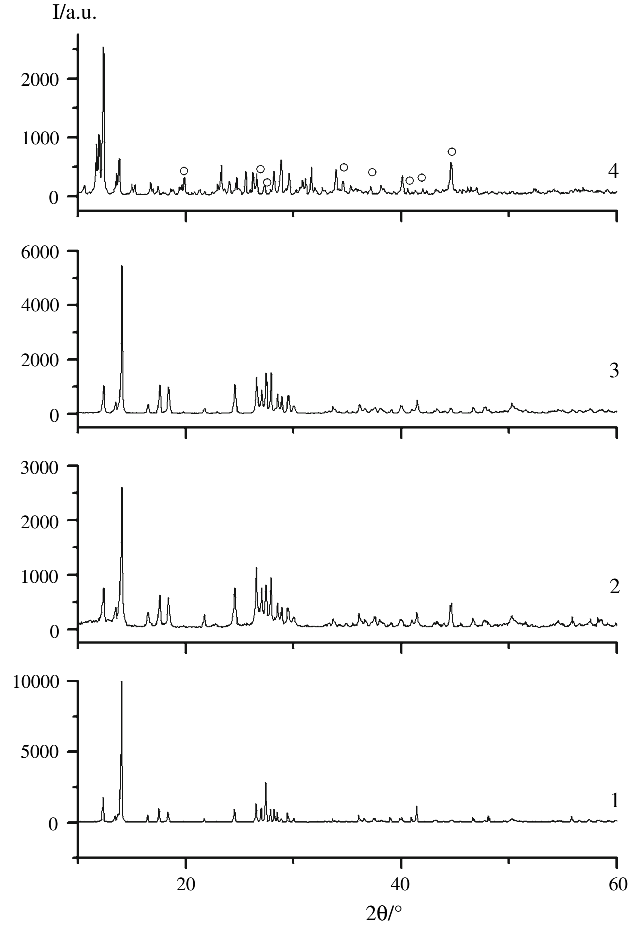

Fig. 1 Diffractograms of initial ADM salt (*1*) and that subjected to MChT for 120 min in air (*2*), in ethanol (*3*), and in water (*4*). The reflexes belong to: °, Mo_4O_{11}

$$2(NH_4)_2Mo_2O_7 = 3MoO_3{\cdot}2NH_3{\cdot}H_2O + MoO_{3(h)} + 2NH_3 + H_2O \qquad (2)$$

Appearance of hexagonal MoO_3 is a consequence of the influence of ammonium ions on its crystalline structure during ADM destruction over 200 °C [5, 12]. As a result of ammonia removal from the structure of hexagonal MoO_3 at temperature over 300 °C that is easily transformed into rhombohedral MoO_3.

For the initial ADM the theoretical value of mass loss in two-first stages of heating (i.e., about 205–215 and 250 °C) $\Delta m_{1,2}$ is 7.65% w/w while the experimental one—7.3% w/w. The third stage of decomposition at 280–340 °C ends with formation of rhombohedral MoO_3 according to the reaction:

$$3MoO_3{\cdot}2NH_3{\cdot}H_2O = 3MoO_{3(r)} + 2NH_3 + H_2O \qquad (3)$$

with the same theoretical mass change (7.65% w/w) but the experimental one is equal to 6.9% w/w. Analogous results for the third stage of thermolysis were obtained also for the ADM samples after their milling in air and ethanol.

Mechanochemical activation of ADM in water leads to its hydration, i.e., to 4-aqueous ammonium paramolybdate (APM) formation (ASTM N 70-1707) (Fig. 1, diffractogram 3). It should be noted that such experimental fact was not described in literature earlier. Interestingly, that both usual immersion of ADM in water and its hydrothermal treatment at 100–300 °C does not result in APM making. Four endothermal effects with the minima at 120, 200, 230, and 325 °C are observed on the DTA curves for this sample (ADM–MChT-w) (Fig. 2). The comparison of DTA data and the corresponding results of the XRD allows to suggest the following scheme of thermal decomposition of the ADM–MChT-w sample:

1. In the first stage in the temperature range 90–130 °C dehydration—cleavage of 4 water molecules takes place; whereby the theoretical mass loss is 5.8% w/w, the experimental value—5.65% w/w.
2. Stages 2 and 3 which are difficult to separate proceed in the temperature range 190–240 °C and according to the XRD they end with transformation of anhydrous APM into the phase of the composition $(NH_4)_2O$-$Mo_{2.5}O_{7.5}$ (ASTM N 26-77) accordingly the reaction:

$$(NH_4)_6Mo_7O_{24} = 2(NH_4)_2OMo_{2.5}O_{7.5} + 2NH_3 + H_2O \qquad (4)$$

3. The fourth stage of decomposition proceeds in the temperature range 280–330 °C and results in formation of rhombohedral molybdenum trioxide according to the scheme:

$$2(NH_4)_2OMo_{2.5}O_{7.5} = 5MoO_3 + 5NH_3 + 2H_2O \qquad (5)$$

Thus, stages 2–4 cause the values $\Delta m_{\text{theor}} = 12.6\%$ w/w and $\Delta m_{\text{exp}} = 12.3\%$ w/w.

It should be added that besides rhombohedral MoO_3 the reflexes related to partially reduced molybdenum oxide namely, Mo_4O_{11} (ASTM N 13-142) are present on the diffractograms of the products of complete thermal decomposition for the sample ADM–MChT-w (on Fig. 1 of Mo_4O_{11} reflexes were marked by symbol °) which is understandable because evolving ammonia acting as a reducing agent is present in the system.

Taking the said reactions into account the total theoretical mass loss for the sample ADM–MChT-w should be 18.4% w/w but that determined experimentally from the TG curve is equal to 18.6% which is in good agreement.

The summarized data of step-by-step decomposition for the initial ADM and that modified using MChA in different media are presented in Table 1.

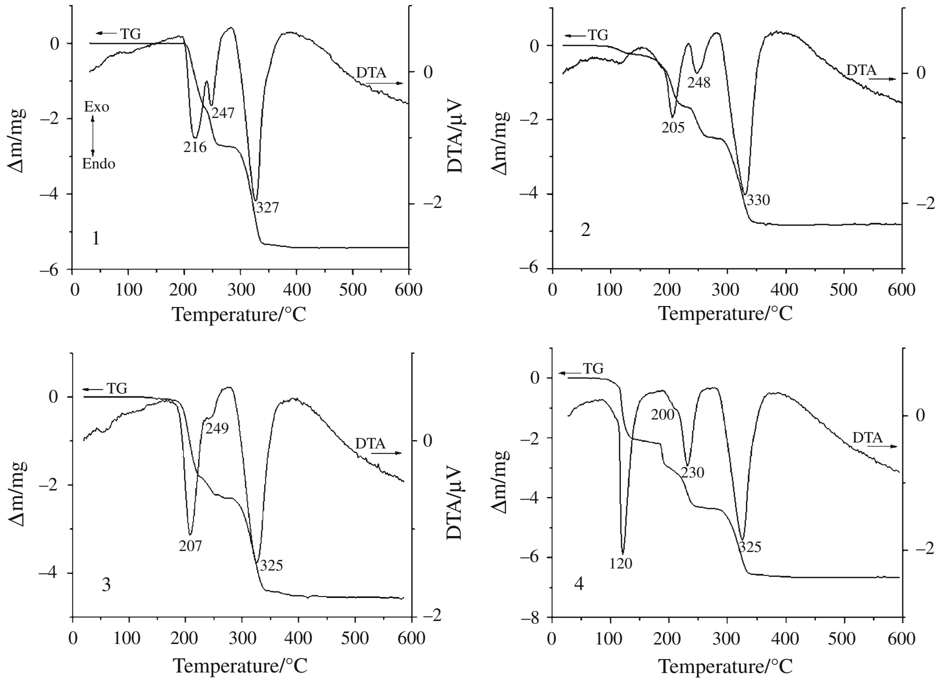

Fig. 2 DTA and TG curves for the initial ADM (*1*) and after MChT for 120 min in air (*2*), ethanol (*3*), and water (*4*)

Table 1 The results of thermal decomposition of the initial ADM and that after MChA in various media (data of thermal analysis and XRD)

MChT conditions	XRD		Mechanism
	Transient phase	Final phase	
Without MChT	$3MoO_3{\cdot}2NH_3{\cdot}H_2O$, $MoO_{3(h)}$	ADM, $MoO_{3(r)}$	*Stages 1 and 2*:
Air			$2(NH_4)_2Mo_2O_7 = 3MoO_3{\cdot}2NH_3{\cdot}H_2O + MoO_{3(h)} + 2NH_3 + H_2O$
Ethanol			*Stage 3*:
			$3MoO_3{\cdot}2NH_3{\cdot}H_2O = 3MoO_{3(r)} + 2NH_3 + H_2O$
Water	$(NH_4)_2OMo_{2,5}O_{7,5}$	APM, Mo_4O_{11} $MoO_{3(r)}$	*Stage 1*:
			$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O = (NH_4)_6Mo_7O_{24} + 4H_2O$
			Stages 2 and 3:
			$(NH_4)_6Mo_7O_{24} = 2(NH_4)_2OMo_{2,5}O_{7,5} + 2NH_3 + H_2O$
			Stage 4:
			$2(NH_4)_2OMo_{2,5}O_{7,5} = 5MoO_{3(r)} + 4NH_3 + 2H_2O$

Mechanochemical treatment of V_2O_5

The results of MChA of pure vanadium pentoxide are generally in agreement with the results obtained earlier [17]. However, we used a mill of smaller energetic charge (600 rpm in comparison with 3,000 rpm in [17]). It should be noted that under these conditions of treatment (600 rpm) the phase transformations in V_2O_5 do not occur (Fig. 3). Only changes of intensity of reflexes corresponding to different crystalline planes and their shifts (slight change of interplanary spacings) are observed on the diffractograms of this mechanochemically treated oxide. Besides, V_2O_5 amorphization is a general trend (particularly noticeable after its MChT in air) which can be seen in decrease of intensity of all reflexes compared to the initial sample and in appearance of stronger background on the diffractograms.

In our opinion the shape of DTA and TG curves for the V_2O_5 sample milled in water is interesting (Fig. 4). Thus, no thermal effects up to the melting point (695 °C) and no mass loss are observed for the initial oxide. However, mass loss on the TG curve in the temperature range 200–400 °C for the sample undergone MChA reaches 1.2% w/w that equals approximately 0.06 mol H_2O/mol V_2O_5 (counting on weight of V_2O_5 without adsorption of water which is removed at 20–200 °C). Besides three diffused endoeffects at 230, 315, and 390 °C on DTA-curve (Fig. 4, curve 2) are present. They obviously correspond to evolving of strongly bonded structural, hypothetically intercalated, water which was introduced into interlayer space of V_2O_5 during

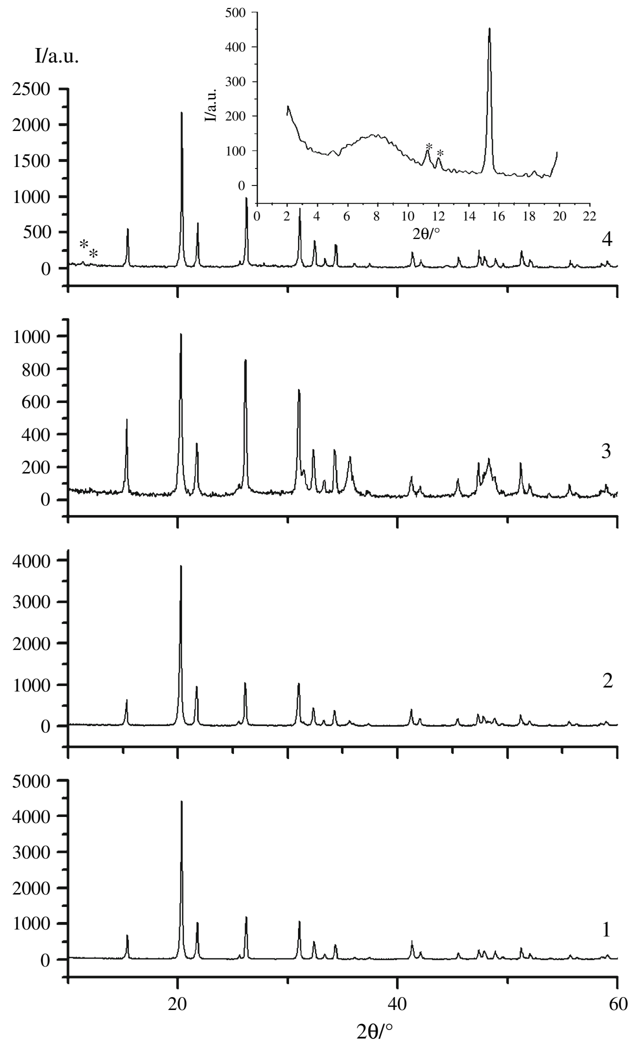

Fig. 3 Diffractograms of initial V_2O_5 (*1*) and that subjected to MChT for 120 min in ethanol (*2*), in air (*3*), in water (*4*)

MChT. Reflexes of low intensity (about 5%) corresponding to the interplanary spacings 0.735 and 0.783 nm appear on diffractogram milled sample (on Fig. 3, curve 4 these reflexes were marked by symbol *) that confirms said above. This experimental fact is remarkable since as it is well known the crystalline V_2O_5 is stable and does not react with water in usual conditions [24].

Mechanochemical treatment of the V_2O_5–$(NH_4)_2Mo_2O_7$ mixture in air atmosphere

The XRD patterns of $V_2O_5/(NH_4)_2Mo_2O_7$ sample subjected to MChT in air indicate the presence of reflexes attributed to starting components. This is the evidence of incomplete decomposition of ammonium salt and the absence of phase transformations during milling of vanadium pentaoxide (Fig. 5). However, for V_2O_5 milled in mixture some changes are observed compared to individual V_2O_5. Thus, in the pure starting oxide the reflex from the crystallographic plane (010), which contains V=O (basal plane) is the most intensive and the ratio $I_{010}/I_{110} = 3.85$, after its MChT in air one equals 1.25. Simultaneously, after MChT within 60 min the peak corresponding to the plane (110) is characterized by the maximal intensity and the value I_{010}/I_{110} equals in 0.95. This ratio reduces to 0.72 with the increasing of milling time up to 120 min. Thus, as a result of MChA in air, surface concentration of the vanadyl plane (010) decreases. At the same time, changes of relative intensities of other lines of V_2O_5 are also observed. Intensity of ADM reflexes also diminishes. For example, relative intensity of the strongest reflex from the ADM plane (101) after MChT for 60 min is 96%, but for 120 min only 43% in comparison with those for initial mixture. The difference between the XRD for given compounds in mixture and that for pure components can be explained by interaction of components in the activation process. Changes in the crystalline structure of vanadium pentoxide at treatment can occur, e.g., due to the influence of ammonia and water evolving during decomposition of ADM. After dry milling sufficiently strong amorphization of the components is observed as indicated small halos on the diffractograms, the strongest of which is in the range $2\Theta = 22$–$35°$.

The FTIR data also indicate interaction of components of V_2O_5/ADM mixture during their MChA (Fig. 6). The IR

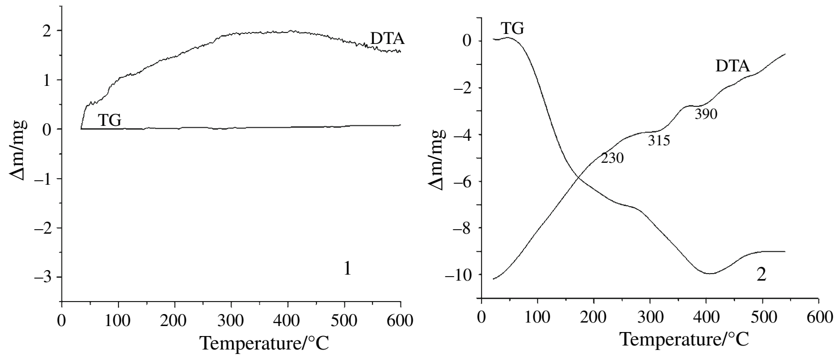

Fig. 4 DTA and TG curves for the initial V_2O_5 (*1*) and that subjected to MChT for 120 min in water (*2*)

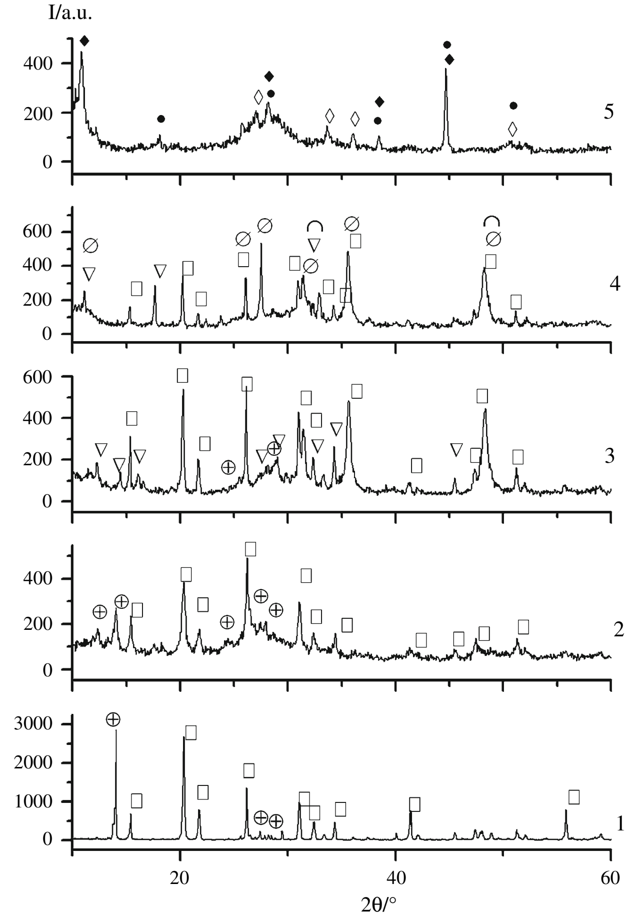

Fig. 5 Diffractograms of the initial $V_2O_5/(NH_4)_2Mo_2O_7$ mixture (*1*) and after MChT in air for 120 min (*2*), in ethanol (120 min) (*3*), in water (60 min) (*4*), and 240 min in water (*5*). The reflexes belong to: □, V_2O_5; ⊕, ADM; ∅, APM; ∇, $MoO_{2.8}$; ◇, $HMoO_3{\cdot}2H_2O$; ●, $(NH_4)_2Mo_4O_{13}$; ∩, χ-Mo_8O_{23}; ◆, $(NH_4)_2V_6O_{16}{\cdot}1.5H_2O$

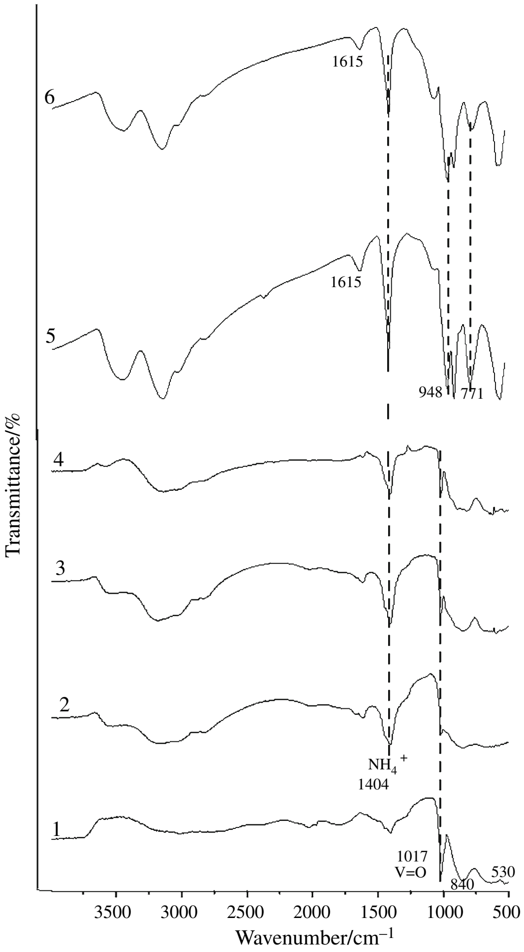

Fig. 6 FTIR spectra for initial V_2O_5 (*1*), the unmodified system $V_2O_5/(NH_4)_2Mo_2O_7$ as well as mechanochemically modified in air 120 min (*2*), ethanol 120 min (*3*), and water for 120 min (*4*), 240 min (*5*), and 360 min (*6*)

spectrum of the initial V_2O_5 are characterized by the presence of absorption bands at 530 (*ν* V–O), 628, 840 (–V–O–V–), 1017 (V=O) cm^{-1} [25]. The spectra of the vanadium–molybdenum composition after the MChT in air for 60 and 120 min are similar to each other. The shift of absorption band from V=O into the region 1,021 cm^{-1} is observed. The band corresponding to the vibrations of bridge bond –V–O–V– shifts toward 845 (60 min) and 850 cm^{-1} (120 min). The intensive band at 1,404 cm^{-1} assigned to the vibrations of the NH_4^+ groups is also present in the spectrum [26]. Additionally, the next absorption bands appear: of low intensity at 983 cm^{-1} which can be referred to the privileged coordination of binary bonded oxygen with molybdenum atoms (thus, in MoO_3 the vibrations Mo=O are observed in the region 995 cm^{-1} [23]) and the shoulder of low intensity at 930 cm^{-1} which, according to [27], is responsible for the structure of monomolybdates. It should be stressed that the quoted IR spectroscopy data are in good agreement with those obtained earlier for the V_2O_5/MoO_3 system with the analogous ratio of oxides [3, 15, 28].

Mechanochemical treatment of the V_2O_5–$(NH_4)_2Mo_2O_7$ mixture in ethanol

Compared to the MChA in air grinding in ethanol is characterized by both similarities and differences. The likeness includes the fact that according to the XRD the initial substances—ADM and V_2O_5 are present in the products obtained via treatment of $V_2O_5/(NH_4)_2Mo_2O_7$ mixture in ethyl alcohol (Fig. 5). At the same time, the intensity of the strongest peak of ADM from the plane (101) after milling for 60 min is 92% but for 120 min—60% in comparison with those for initial salt. Vanadium pentaoxide does not undergo phase transformations during MChA in ethanol (as it was during dry grinding).

There are some experimental facts indicating differences of MChT in the two above mentioned media. Firstly, the reflexes of partially reduced molybdenum oxide—$MoO_{2.8}$ phases (ASTM N 9-195) are present on the diffractograms of milled products whereby with the increase of activation time from 60 to 120 min its content in the products does not change (based on the intensity of the strongest line corresponding to the interplanary spacing 0.336 nm). Reduction of molybdenum trioxide, formed during ADM decomposition, to $MoO_{2.8}$ may be connected with the presence in the system of another reducing agent (besides ammonia), namely, ethanol. This fact agrees with literature data. For example, authors of [24] also reported about formation of such compounds as bronzes at milling of MoO_3 in hydrocarbon media. Secondly, for a given medium (ethanol) after 60 min of treatment intensity ratio of the reflexes V_2O_5 I_{010}/I_{110} is the same as for the those in starting mixture but longer treatment (120 min) promotes the increase of relative content of vanadyl plane (intensity of (010) V_2O_5 reflection) on the surface of samples of 20% (a reverse tendency is observed during MChT in air). The obtained result can be explained by anisotropic deformation of V_2O_5 by breaking of vanadium oxide layers parallel to the plane (010). As shown earlier [17] treatment of pure V_2O_5 in ethanol also leads to anisotropic deformation of crystal and increase of relative content of the plane (010) on the oxide surface. Thirdly, amorphization of the system components at grinding in ethanol is not practically observed.

Shift to 1,025 cm^{-1} of the absorption band corresponding to vibrations of the V=O bond (as in the case of MChA in air) is observed in the IR spectrum of the V_2O_5/ADM sample after its MChT in ethanol (Fig. 6) whereas the band concerning to the vibrations of the bridging bond –V–O–V– (842 cm^{-1}) remains the same as for the individual V_2O_5. The intensive absorption band at 1,406 cm^{-1} is also present in the spectrum.

Mechanochemical treatment of the V_2O_5–$(NH_4)_2Mo_2O_7$ mixture in water

The most essential changes in the structure of the compounds of mixture and the strongest interaction of its components were observed during milling in the aqueous medium. As in the two above-described cases, chemical and phase transformations of the vanadium pentaoxide/ADM composition during MChT in water were studied by means of XRD and thermal analyses as well as IR spectroscopy. During water treatment of salt (ADM) in mixture as shown above for individual salt its hydration (transformation into 4-aqueous ammonium paramolybdate—APM) and formation of molybdenum trioxide take place according to:

$$4(NH_4)_2Mo_2O_7 + 4H_2O = (NH_4)_6Mo_7O_{24}\cdot 4H_2O + 2NH_3 + MoO_3 + H_2O \quad (6)$$

In the presence of evolving ammonia MoO_3 can reduce, e.g., in accordance with the reaction (as in the case of MChT in ethanol):

$$MoO_3 = MoO_{2.8} + 0.1O_2 \quad (7)$$

Taking the XRD into account one can think that MChT of the mixture for 60 min leads to formation of APM according to (6). Besides, the reflexes of vanadium pentoxide and two nonstoichiometric molybdenum oxides ($MoO_{2.8}$ and χ-Mo_8O_{23}—ASTM N 5-339) can be seen on the diffractograms of the treated composition (Fig. 5, curve 4). Thus, during its grinding in water for 60 min vanadium pentaoxide (contrary to ADM) does not undergo phase and chemical transformations as it was also observed at MChT of pure V_2O_5 under the same conditions. Only partial hydration of vanadium pentaoxide is possible but without change of chemical composition and crystalline structure. Thus, above it was showed that on the TG curve of individual V_2O_5 modified in water (Fig. 4) there can be distinguished two stages of mass loss (at 85–215 and 270–395 °C). This mass loss can be connected with removal of adsorbed and strongly bonded water retained on the surface by crystalline structure defects or intercalated in the interlayer space.

On the other hand, for the individual ADM sample subjected to milling in water mass loss on the TG curve consists from some stages and comes to the end at 400 °C (Fig. 2, curve 4). Hence taking the registered phase composition of mechanochemically treated mixture into account, mass loss is possible, first of all, due to APM destruction (according to Eq. 8) and partially due to water removal from the V_2O_5 surface.

$$(NH_4)_6Mo_7O_{24} = MoO_3 + 6NH_3 + 7H_2O \quad (8)$$

The TG and DTA curves for the mixture undergone MChT in the aqueous medium for 60 min differ from the corresponding curves obtained for pure components (Fig. 7). They are characterized by:

(i) the presence of narrow pronounced endothermal effect in the temperature range 40–120 °C with the minimum at 90 °C ($\Delta m_{1exp} = 5.06\%$ w/w)—this is the loss of weakly bonded adsorbed water and also one located in the porous space. This suggestion is supported by the fact that the quantity Δm_{1exp} exceeds four times its total value of mass loss which is observed in this temperature interval for pure milled V_2O_5 and ADM;

(ii) mass loss in the temperature range 120–400 °C is relatively gradual. It corresponds to decomposition of

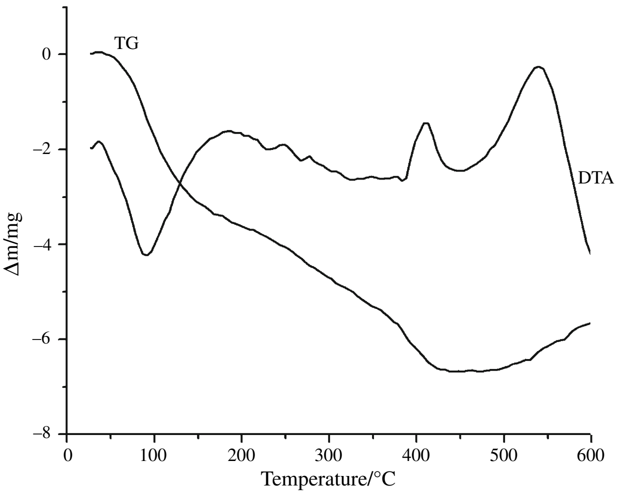

Fig. 7 DTA and TG curves for the $V_2O_5/(NH_4)_2Mo_2O_7$ system after MChT in water for 60 min

APM and removal of strongly bonded water from the surface of mechanochemically modified V_2O_5; $\Delta m_{2\text{exp}} = 8.27\%$ w/w and $\Delta m_{2\text{teor}} = 8.15\%$ w/w; the latter value consists of mass loss calculated from Eq. 8 and that for range temperature 120–400 °C for the milled individual V_2O_5;

(iii) increase of mass at 430–600 °C ($\Delta m_{3\text{exp}} = 2.09\%$ w/w and $\Delta m_{3\text{theor}} = 2.27\%$ w/w from Eq. 7) can be explained by oxidation of nonstoichiometric molybdenum oxides formed during MChT (from reverse reaction (7)). Taking the quantity $\Delta m_{3\text{exp}}$ into account the amount of such oxides was determined: their contents in the milled products were about 10% mass. Considering equations of reactions (6) and (7) and proportion of components in the initial mixture (V:Mo = 0.7:0.3) only, half of nonstoichiometric molybdenum oxides can be formed according to these reactions but the other half possibly according to the following reaction of ADM decomposition occurring during MChT:

$$(NH_4)_2Mo_2O_7 = 2MoO_{2.8} + 2NH_3 + H_2O + 0.7O_2 \tag{9}$$

As follows from our calculations, about 5% w/w of ADM undergoes transformation in conformity with reaction (9).

Thus, based on some data obtained using various physicochemical methods it can be concluded that transformations proceed according to reactions (6)–(9) during MChA of the V_2O_5 and ADM mixture in water for 60 min. Their products contain 54% w/w vanadium pentoxide, 36% w/w 4-aqueous ammonium paramolybdate and 10% w/w nonstoichiometric molybdenum oxides.

Interesting results were obtained through milling of $V_2O_5/(NH_4)_2Mo_2O_7$ in water during longer time (240 and 360 min) (Fig. 5). Thus, there were such changes of the properties of the system: reflexes of V_2O_5 phase disappear from diffractograms and new peaks related to the ammonium-containing vanadium-oxide and molybdenum-oxide phases namely: $(NH_4)_2V_6O_{16}\cdot1.5H_2O$ (ASTM N 51-376) and $(NH_4)_2Mo_4O_{13}$ (ASTM N 50-608) as well as of the compound with formula $HMoO_3\cdot2H_2O$ (ASTM N 38-65) are revealed. It should be noted that formation of $(NH_4)_2V_6O_{16}\cdot1.5H_2O$ agrees with results of article [29] where compound having similar composition namely, $(NH_4)_2V_{12}O_{31}\cdot nH_2O$ and which is formed as a result of ammonia and hydrated xerogel $V_2O_5\cdot nH_2O$ interaction was found.

Table 2 Interlayer distances in V_2O_5 and $V_2O_5/(NH_4)_2Mo_2O_7$ after MChT in water

System	Treatment time/min	d/nm
V_2O_5	0	0.574
V_2O_5	60	0.575
V_2O_5	120	0.735; 0.783
$V_2O_5/(NH_4)_2Mo_2O_7$	60	0.925; 1.154
$V_2O_5/(NH_4)_2Mo_2O_7$	120	0.797; 1.132

It is worth noting that after MChT of the mixture $V_2O_5/(NH_4)_2Mo_2O_7$ in water on diffractograms reflexes which correspond to significantly increased (in some cases twice) interlayer distances compared to the regular lattice of starting V_2O_5 appear (Table 2). It is known that vanadium pentaoxide is capable of dissolving in water during MChT and forming hydration complexes of polyvanadium acids $H_2V_{12}O_{31}\cdot nH_2O$ [30]. The presence of chemically bonded water is confirmed by appearance of absorption bands at 1,640 and 3,600 cm^{-1} in the IR spectra [31]. Articles [32, 33] present a laminar model of the $V_2O_5\cdot nH_2O$ structure and show that the distance between planes (between layers) can increase from 0.8 nm ($n = 0.1$–0.5) to more than 4.0 nm ($n = 18.5$). Particularly, the interlayer distance is equal to 1.157 nm for the structure $V_2O_5\cdot1.6H_2O$.

Interlayer distance is determined, first of all, by the strength of water molecule interactions with vanadium–oxygen layers through hydrogen bonds. During grinding in the aqueous medium it is possible to separate layers due to mechanical action and to introduce water molecules into the interlayer space which promotes to increase in the interplanar (interlayer) distances.

One can suppose that in the presence of ammonia evolved during ADM decomposition which is also capable of penetrating the interlayer space of V_2O_5 [30], intercalation process is more probable and, as a result, plane separation is intensified. This version can be verified by comparison the value of interlayer distance for pure vanadium oxide and that subjected to MChT in water.

As shown above for V_2O_5 milled in water it is 0.735 and 0.783 nm. On the other hand, the interlayer distance is equal to 0.925–1.154 nm for the V_2O_5 s prepared using water milling of mixed sample (Table 2).

In the IR-spectra of the samples $V_2O_5/(NH_4)_2Mo_2O_7$ after their MChT in water shift of absorption band from 1,017 to 1,021 cm^{-1} (for 60 and 120 min, respectively) corresponding to vibrations of the V=O bond is observed which indicates strengthening of the terminal bond V=O and its complete disappearance after treatment during 240 and 360 min.

Moreover, with the increase of milling time of $V_2O_5/(NH_4)_2Mo_2O_7$ samples in water (up to 240 and 360 min) additional intensive absorption bands at 771 and 948 cm^{-1} also appear in the IR spectrum. They characterize the Mo–OH bond related to molybdenum hydrates of the compound $HMoO_3{\cdot}2H_2O$ which is in agreement with the literature data [34] and the above-described results obtained by means of the XRD method.

The intensive absorption band observed in all cases in the range 1,401–1,410 cm^{-1} is assigned to the presence of NH_4^+ group but occurrence of absorption bands in the range 1,616–1,621 cm^{-1} (deformation vibration) and 3,590 cm^{-1} (stretching vibration)—to the presence of water in the samples.

Conclusions

This article presents the course of topochemical reactions in the composition $V_2O_5/(NH_4)_2Mo_2O_7$ enriched in vanadium and initial components and other physicochemical transformations during their MChT in different media. It was shown that mechanisms of thermodestruction for starting ammonium dimolybdate and for one after milling in air and ethanol are identical. But for ADM treated in water this mechanism differs. After MChA of the $V_2O_5/(NH_4)_2Mo_2O_7$ system with the change of medium various products are obtained. Thus, MChA of $V_2O_5/(NH_4)_2Mo_2O_7$ in air and ethanol does not lead to the change of phase composition. However, the structure of vanadium pentaoxide in milled composition is different: in air the preferred surface orientation of plane (110), in ethanol–vanadyl plane V=O (010) is achieved. Maximal interaction of mixture components are observed during MChT in water. With the grinding time 60–120 min, on the one hand, incorporation of water molecules and ammonia into the interlayer space of V_2O_5 (both pure and in the mixture with ADM) with the significant increase of interlayer distances and, on the other hand, hydration of ammonium dimolybdate with its transformation into 4-aqueous ammonium paramolybdate and formation of nonstoichiometric molybdenum oxides take place. During activation in water for 240–360 min the V_2O_5 phase disappears and vanadium and molybdenum oxide phases which contain ammonium are formed. It is noted that intermediates synthesized by mechanochemical route can be considered as precursors for preparation of V–Mo–O catalysts.

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