

## Solid-state interactions of vanadium and phosphorus oxides in the closed systems

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**Abstract** Physicochemical processes during thermal treatment of vanadium and phosphorus oxides mixture (1) as well as with diammonium hydrophosphate (2) in the closed system (autoclave) have been studied. In the first case, at 300 °C, the defective structure  $\gamma$ -VOPO<sub>4</sub> is formed and in the second case, there was established possibility of synthesis of vanadyl hydrophosphate—the precursor of vanadyl pyrophosphate (the catalyst of *n*-butane oxidation to maleic anhydride). At the same time, various phases of mixed ammonium and vanadium phosphates were obtained at lower and higher temperatures.

**Keywords** Solid-state interaction · Vanadium phosphates · Closed system

### Introduction

The vanadium–phosphorus oxide system is interesting from both theoretical point of view since numerous phases were found in this system [1–7] and practical one because individual substances, mainly vanadyl pyrophosphate (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (VPP) and its precursor—semihydrate vanadyl hydrophosphate, VOHPO<sub>4</sub>·0.5H<sub>2</sub>O (VHP) are effective catalysts of selective hydrocarbons oxidation [3–6].

Though long time ago [1, 3] perspective of application of vanadium phosphates synthesis carried out in the solid phase in order to obtain condensed phosphates was pointed out, so far the reactions of this type in the vanadium oxides–phosphorus pentaoxide system (or orthophosphoric acid salts) have been insufficiently studied. There can be reported other studies on this subject, i.e.,

- formation of glass in the mixture V<sub>2</sub>O<sub>5</sub>–P<sub>2</sub>O<sub>5</sub> where diammonium hydrophosphate was chosen as a source of phosphorus [8];
- interaction of vanadium pentaoxide with orthophosphoric acid at 530 °C [9];
- reactions between V<sub>2</sub>O<sub>4</sub> and P<sub>2</sub>O<sub>5</sub> carried out in order to prepare catalysts [10];
- preparation of vanadyl pyrophosphate from ammonium metavanadate and ammonium dihydrophosphate in the temperature range 550–850 °C in the CO<sub>2</sub> stream [11];
- formation of such phases as (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, V<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>, VO(PO<sub>3</sub>)<sub>2</sub>, VO(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> in the VO<sub>2</sub>–P<sub>2</sub>O<sub>5</sub> system at 900 °C at different cooling rate and in various media [12];
- synthesis of mixed ammonium–vanadium phosphates from vanadium pentaoxide and diammonium hydrophosphate at 280–340 °C in air atmosphere [13–15] and also formation of other binary vanadium phosphates [16–18]. However, all these enumerated investigations are not systematic. Only formation of VPO-phases during interaction in air atmosphere in the system V<sub>2</sub>O<sub>5</sub>–NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> was studied in detail [3, 19]. Moreover, all these investigations were carried out in open systems, i.e., under the conditions in which gaseous products are removed from the reaction zone, which in the authors' opinion [3, 19] does not promote attainment

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of the equilibrium state. At the same time, solid-state reactions in open systems now remain perspective technique for synthesis heterogeneous catalysts [20] and phosphates [21].

The aim of this article is to study the alternative way of preparation of vanadium–phosphate catalysts—the hemihydrate vanadyl hydrophosphate (VHP)  $\text{VOHPO}_4 \cdot 0.5 \text{H}_2\text{O}$ , the precursor of vanadyl pyrophosphate (VPP), by means of synthesis in the solid phase in closed system.

## Experimental

For systematic studies the following systems there were chosen:  $\text{V}_2\text{O}_5-(\text{NH}_4)_2\text{HPO}_4$  (system 1),  $\text{VO}_2-(\text{NH}_4)_2\text{HPO}_4$  (system 2),  $\text{NH}_4\text{VO}_3-(\text{NH}_4)_2\text{HPO}_4$  (system 3). It should be emphasized that both diammonium hydrophosphate and ammonium metavanadate begin to decompose before achieving of melting temperature [22, 23]. Therefore, in all the studied mixtures at temperatures up to 400 °C, the reactions proceed in the solid phase, i.e., without the formation of liquid phase as opposed to the interactions in the systems including ammonium dihydrophosphate, where already at 200 °C its melting is observed [2, 3, 19]. The important factor for choosing the above-mentioned substances as substrates was the Hedwall effect according to which reactivity of solid is increased in statu their decomposition [24–26].

The  $P/V$  ratio in the reaction mixture in all cases was 1.15 as it usually takes place in the synthesis of catalysts of this type [2–6, 10]. All of the chemicals used in this investigation were of analytical grade (Fluka).

The synthesis in the solid phase was carried out for 3 h at 200–400 °C in the closed system, i.e., in the steel autoclave with quartz inserts in the atmosphere of volatile products of reagents decomposition (ammonia, steam). Pressure of ammonia in the experiments was 0.3–8.0 MPa.

As follows from the studies, the molar ratio of ammonia/vanadium oxide is more important characteristic affecting component interaction in the chosen systems than ammonia pressure. As known, the presence of ammonia in the gaseous phase promotes reduction of  $V(5+)$  to lower oxidation degrees [19].

Carrying out solid-state reactions in closed systems, namely in autoclaves, may be also useful in explanation of dry mechanochemical activation mechanism, since in both the cases solids are subjected to the action of high pressures [25].

Before the experiment, the mixtures of initial substances were ground in the agate mortar. However, then the grinded substances were not pressed as it often occurs while carrying out reactions in the solid state [24].

The thermal analysis of prepared samples was made using the derivatograph Q-1500D (MOM Budapest) in the temperature range 20–800 °C, the heating rate of samples in air was 10°/min. It should be noted that thermogravimetric measurements are very informative at investigations of both structure of VPO system and various their transformations [12, 13, 27–30]. The powder X-ray diffraction (XRD) patterns were recorded on the diffractometer DRON-4 (Russia) with  $\text{CuK}\alpha$  radiation. The IR spectra were measured using the spectrometer Specord M80 in the mode of two-beam measurement (tablets with KBr). The specific surface area  $S$  was determined by method of argon thermal desorption applying the apparatus GCh-1 (the firm, Chromatographia, Russia). Total acidity of samples was calculated from the adsorption data of pyridine measured using the gas chromatography method [31].

## Results and discussion

The reactions of air dried samples of vanadium pentaoxide and dioxide as well as of ammonium metavanadate with phosphorus pentaoxide at 300 °C were preliminarily studied. Choice of this temperature is explained by the fact that it exceeds the Tamman temperature (which is 0.35–0.40  $T_{\text{melt}}$  for all oxides). Under these conditions, selfdiffusion processes in solids which are important for interaction in the solid phase become sufficiently intensive [25]. On the other hand, already at 347 °C  $\text{P}_2\text{O}_5$  the sublimation starts. Due to it, in closed systems, the possibility of mass transfer through the gaseous phase appears.

The data of XRD (Table 1) can be interpreted as follows: in all reaction systems, there is formed practically pure (though with structural defects) phase of one of vanadium (5+) phosphates, i.e.,  $\gamma$ -form. Earlier in this system formation of  $\alpha$ - $\text{VOPO}_4$  and one of condensed phosphates, i.e.,  $(\text{VO})_2\text{P}_2\text{O}_{13}$  was observed at 300 °C [32]. It should be noted that obtaining of  $\gamma$ - $\text{VOPO}_4$  at such low temperature (300 °C) was found for the first time by us because, as a rule, this phase is one of the intermediate products of thermal transformation in oxygen (at 580 °C) of vanadyl hydrophosphate [4, 5]. The distinctive feature of crystalline structure of  $\gamma$ - $\text{VOPO}_4$  prepared by us using the solid-state method are unusual intensity ratios of  $I/I_0$  (ratio of the reflection intensity from given plane to the intensity of the strongest reflection) on the diffractograms. Thus, XRD peak corresponding to the plane (332) is the most intensive in all three systems while the reflection from the plane (221) which, according to literature data, is basic for this phase [4, 5] in these reaction products for the mixtures  $\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$  and  $\text{VO}_2-\text{P}_2\text{O}_5$  is not registered. There are also some other discrepancies of the results described earlier in literature and presented in columns 2, 3 in Table 1

**Table 1** XRD for  $\gamma$ -VOPO<sub>4</sub>, obtained from vanadium and phosphorus oxides in autoclave at 300 °C

Data [4] <sup>a</sup>			V <sub>2</sub> O <sub>5</sub> -P <sub>2</sub> O <sub>5</sub>		V <sub>2</sub> O <sub>5</sub> -P <sub>2</sub> O <sub>5</sub> with NH <sub>3</sub>		VO <sub>2</sub> -P <sub>2</sub> O <sub>5</sub>		NH <sub>4</sub> VO <sub>3</sub> -P <sub>2</sub> O <sub>5</sub>	
hkl	<i>d</i>	<i>l</i> l <sub>o</sub>	<i>d</i>	<i>l</i> l <sub>o</sub>	<i>d</i>	<i>l</i> l <sub>o</sub>	<i>d</i>	<i>l</i> l <sub>o</sub>	<i>d</i>	<i>l</i> l <sub>o</sub>
					0.768 <sup>b</sup>	80				
102	0.616	7	0.614	20						
			0.573 <sup>c</sup>	8	0.569	30	0.571	16	0.569	70
031	0.489	67	0.488	60	0.488	73	0.488	78	0.487	72
221	0.391	100			0.392	13			0.393	56
040	0.384	62	0.382	12	0.384	11			0.382	11
230	0.350	62	0.351	23	0.352	22				
213	0.344	11							0.346	16
223	0.321	45			0.319	49	0.319	21	0.322	78
105	0.309	43	0.309	25	0.309	34	0.309	23	0.310	23
311	0.306	57	0.305	78	0.305	84	0.305	75	0.305	72
			0.295 <sup>c</sup>	22	0.294	10	0.295	13	0.294	21
					0.282 <sup>b</sup>	15				
152	0.277	8							0.279	27
332	0.261	4	0.260	100	0.261	100	0.261	100	0.262	100
333	0.249	10	0.248	10	0.247	15	0.248	14	0.250	21
					0.230 <sup>b</sup>	27				
018	0.206	5	0.207	18	0.207	13	0.208	15	0.208	14
108	0.201	9	0.202	23	0.202	15				
405	0.190	9	0.191	47	0.191	44	0.192	47	0.190	50
307	0.186	6	0.187	23	0.186	16	0.187	20	0.187	23

*d* interplanar spacings (nm)

<sup>a</sup> Reflexes from planes (032), (202), (004), (312), (144), (106), (161), (341), (326), (146), (147), (442), (272), which absent in diffractograms of samples synthesized in this work are not presented

<sup>b</sup> NH<sub>4</sub>VO<sub>2</sub>HPO<sub>4</sub> phase

<sup>c</sup> Vanadyl hydrophosphate (VHP) phase

compared with the experimental data of this article (columns 4–11).

As follows from the literature, loss of oxygen due to spontaneous transition of pentavalent vanadium into the state of lower oxidation during heating is characteristic for the system V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub> [1, 3, 8, 19, 33]. In our case, due to carrying out of this process in the closed system, this phenomenon does not practically take place (at least at 300 °C), though the phase of tetravalent vanadium VOHPO<sub>4</sub>·0.5H<sub>2</sub>O (VHP) has been disclosed in the impurity forms. Its appearance is promoted by the water adsorbed on the surface of initial oxides and presented in autoclave (if before experiments oxide mixtures were dried in the autoclave at 150 °C to remove water, the VHP phase was not detected which is clearly seen taking into consideration reactions (2) and (4) given below).

It is inversely, i.e., oxidation of V<sup>4+</sup> takes place and  $\gamma$ -VOPO<sub>4</sub> is formed for the system VO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> which is favoured by oxygen that is in the autoclave. Analysing the obtained XRD data and the literature data it is possible to

write the following model reactions for the studied oxide systems:



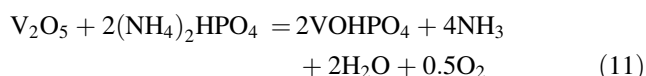
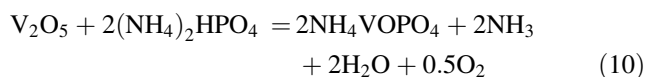
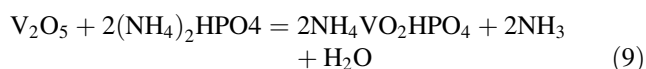
In the second series of experiments, for the same mixtures, water was introduced into the autoclave in the amounts corresponding to the stoichiometry of reactions (2) and (4) as well as ammonia (as a reducing agent). As a result, fraction of vanadyl hydrophosphate increases insignificantly in the products of oxide interaction. Besides, a phase of binary ammonium-vanadium hydrophosphate NH<sub>4</sub>VO<sub>2</sub>HPO<sub>4</sub> (interplanar spacings *d* = 0.768, 0.282, 0.230 nm) which was obtained earlier in the liquid phase [34] and by the hydrothermal method

appears [35]. Moreover, for the system  $\text{NH}_4\text{VO}_3\text{-P}_2\text{O}_5$  the phase of binary ammonium–vanadyl hydrophosphate is basic.

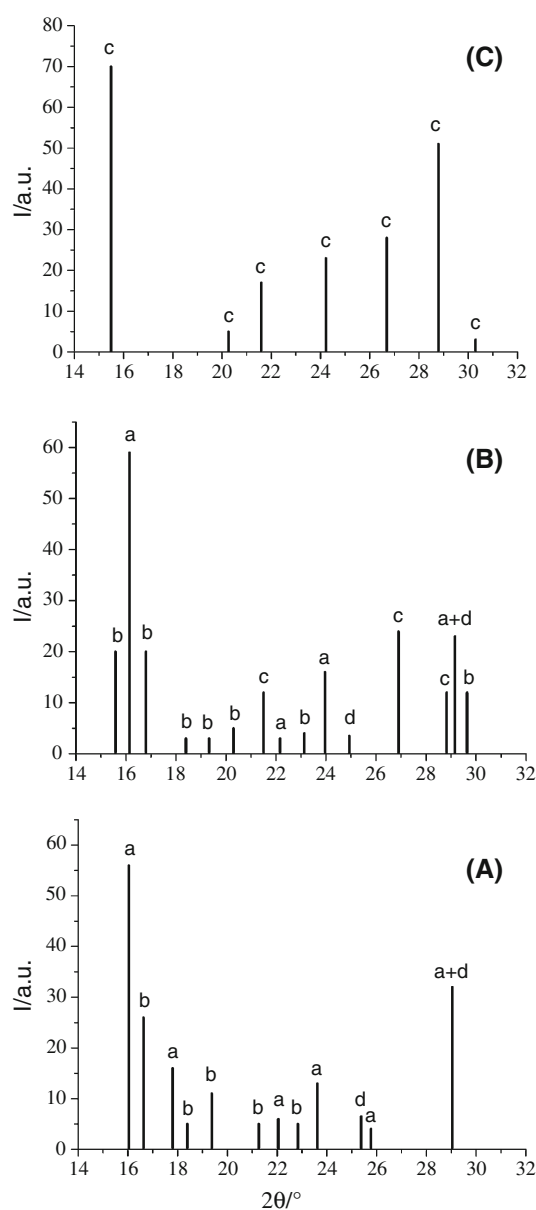
Interaction of vanadium oxides and ammonium metavanadate with diammonium hydrophosphate was studied more systematically. For these mixtures during their heating in the autoclave, direction and rate of reactions should be different from those proceeding in open systems because evolving water and particularly ammonia affect significantly chemical and phase composition, dispersity and other properties of obtained products.

Essential changes were found in the crystalline structure of products of reactions carried out in the autoclave compared to the phase composition of substances prepared by thermal treatment in the open crucible (in air atmosphere). In air with temperature increase there is observed natural tendency for formation of phases of pentavalent vanadium phosphates though large part of oxides does not react even at 400 °C. Interactions in the closed system get complicated because ammonium and vanadium cations are capable of forming numerous phases of complex phosphates [13–15, 36, 37], what is confirmed by XRD spectra (Fig. 1B).

At low temperature (200–250 °C), the reflections corresponding to initial components are registered on the diffractograms of products of reactions carried out also in the autoclave which indicates in particular incomplete decomposition of ammonium salts (Fig. 1A). As follows from the literature [22–24], their thermal decomposition in the presence of ammonia (which takes place in the closed system) is significantly inhibited. On the other hand, evolving ammonia promotes reduction of vanadium oxides and formation of binary phosphates. Thus, on the diffractograms of systems 1 and 3, besides  $\text{V}_2\text{O}_5$ , the reflections of  $\text{VO}_2$ ,  $\text{V}_2\text{O}_4$ , and  $\text{V}_6\text{O}_{13}$  can be observed (Fig. 2A, B). At the same time in the temperature range 200–250 °C basing on stoichiometry it is possible to form the compounds reported in the literature according to the reactions:



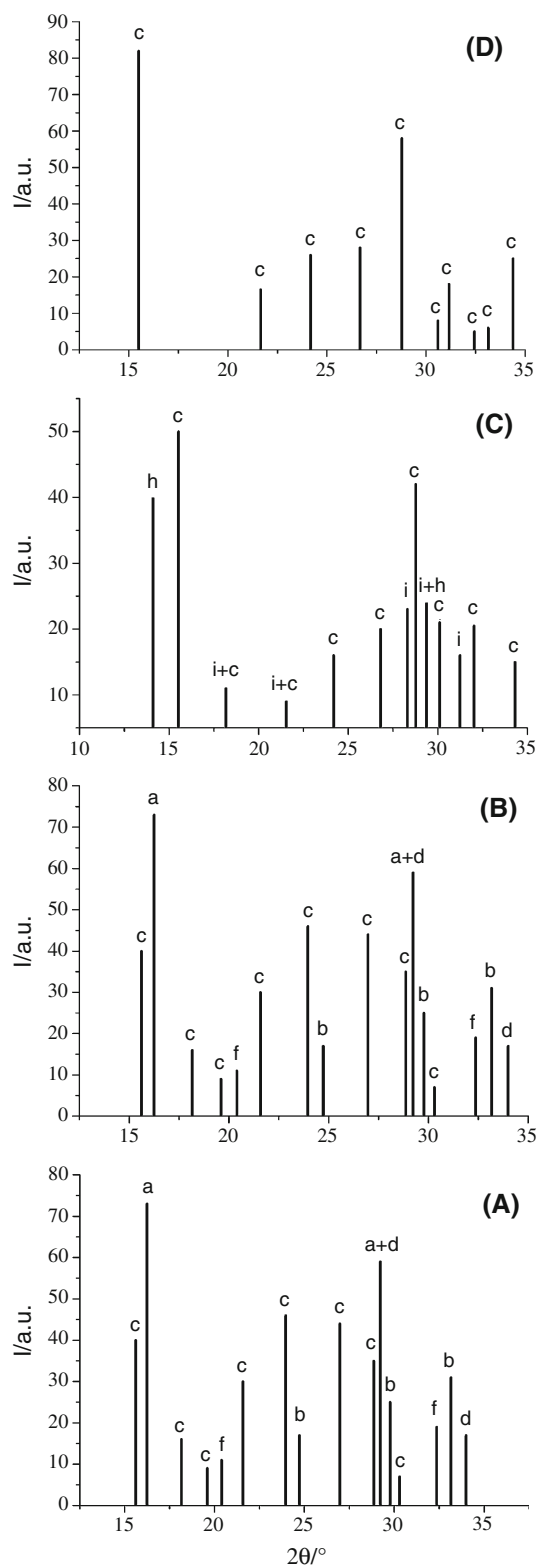
Thus based on the results of XRD (Fig. 1), the reaction (7) proceeds at 200 °C forming mixed ammonium–vanadium



**Fig. 1** Diagrams of system 2 after synthesis at: 200 °C (A), 250 °C (B), 300 °C (C); diammonium hydrophosphate  $(\text{NH}_4)_2\text{HPO}_4$  (a), ammonium–vanadyl phosphate  $\text{NH}_4\text{VOPO}_4$  (b), hemihydrate vanadyl hydrophosphate  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  (c),  $\text{VO}_2$  (d)

(4+) orthophosphate [38] and at 250 °C the reaction (8). The calculations from the DTA and DTG data indicate that in the products of interaction of  $\text{VO}_2$  with diammonium hydrophosphate at 250 °C up to 20% w/w of not decomposed salts, vanadium dioxide, VHP as well as 40% of  $\text{NH}_4\text{VOPO}_4$  are present.

For vanadium pentaoxide (system 1) as well as ammonium metavanadate (system 3) in this temperature range (200–250 °C) the formation of binary phosphates  $\text{NH}_4\text{V}(5+)\text{O}_2\text{HPO}_4$  and  $\text{NH}_4\text{V}(4+)\text{OV}(5+)\text{O}_2(\text{HPO}_4)_2$



**Fig. 2** Diagrams of system 1: with initial  $V_2O_5$  250 °C (A), with  $V_2O_5$  after MChT 250 °C (B), with initial  $V_2O_5$  300 °C (C), with initial  $V_2O_5$  300 °C at excess  $NH_3$  (D), diammonium hydrophosphate  $(NH_4)_2HPO_4$  (a), ammonium–vanadyl phosphate  $NH_4VOPO_4$  (b), semihydrate vanadyl hydrophosphate  $VOHPO_4 \cdot 0.5H_2O$  (c),  $VO_2$  (d),  $V_2O_5$  (f), V/P-mica (h),  $\gamma$ - $VOPO_4$  (i)

1.5  $H_2O$  [5] is characteristic. For the latter system (system 3) their content in the reaction products is smaller because  $NH_4VO_3$  decomposes intensively at only about 300 °C [23].

The most remarkable from obtained results is formation of practically pure VHP at 300 °C for all three studied systems as indicated by the data of XRD (Fig. 1C; Table 2) and differential thermal analysis as well as by IR spectroscopy. Thus all IR spectra of all mentioned samples show the absorption bands characteristic only of VHP: 1105, 1045, 690 and 647  $cm^{-1}$  [5]. As mentioned above, using  $VO_2$  this phase (VHP) is present already after the reaction at 250 °C. However, it is unstable in the ammonium-containing mixture. After thermal vacuum treatment (TVT) up to 300 °C it decomposes or turn into amorphous state (which is unacceptable since its application as a catalyst is accompanied by activation namely through the thermal vacuum treatment [4, 34]).

However, for the system  $V_2O_5$ – $(NH_4)HPO_4$  pure VHP forms at 300 °C only after introduction into reaction zone of the overstoichiometric amount of ammonia (molar ratio  $NH_3/V_2O_5 = 12$ , ammonia pressure = 4.5 MPa) which is indispensable as a reductant (Fig. 2D; Table 2, sample 1).

The same effect can be achieved by the addition to the initial reaction mixture of organic acids: oxalic, citric and salicylic, which were used earlier during the barothermal synthesis of VHP [35]. In their presence at 300 °C, vanadyl hydrophosphate which is even partially transformed into pyrophosphate (reflections corresponding to  $d = 0.386, 0.299, 0.263, 0.239$  nm) is obtained.

Another way of carrying out of solid-state synthesis of VHP from vanadium pentoxide is connected with its mechanochemical activation (MChA). As generally known [25, 39–41], on the one hand, such treatment leads to reduction of activated oxides and on the other hand, it makes its structure more defective which increases the reactivity of oxides. Thus at solid-state interaction  $V_2O_5$ , subjected to MChA in air for 30 min, with diammonium hydrophosphate, the VHP structure is appeared already at 250 °C (Fig. 2B).

It should be noted that the crystalline structure of vanadium hydrophosphate obtained by means of the solid-state reactions differs from that described in literature [4, 5] where the most intensive reflections correspond to the plains (001) and (221) (interplanar spacings  $d = 0.571$  and 0.294 nm). In our case the reflection from the plane (201) ( $d = 0.312$  nm) is the second in respect of intensity, at the same time for VHP synthesized with  $V_2O_5$  and citric acid and also in system 3 after thermal vacuum treatment (samples 3 and 7 in Table 2) the above mentioned reflection is the strongest. Intensity of reflection from the plane (221) for all VHP prepared by means of solid-state reactions is minimal, 5–10%.

**Table 2** Some characteristics of vanadyl hydrophosphate (VHP) phase obtained in autoclave at 300 °C from different mixtures

No	Synthesis condition	Main reflexes ( <i>d</i> / <i>I</i> )	<i>D</i> /nm	<i>S</i> /m <sup>2</sup> g <sup>-1</sup>	<i>C</i> /μmol m <sup>-2</sup>
1	Mixture 1, excess NH <sub>3</sub>	0.571/100; 0.311/71; 0.324/34	21	5	0.082
2	Sample 1 after TVT	0.569/100; 0.311/76; 0.332/33	19	10	0.060
3	Mixture 1 with citric acid	0.312/100; 0.573/94; 0.364/47	26	9	0.094
4	Mixture 2	0.571/100; 0.310/74; 0.332/44	20	4	0.074
5	Sample 4 after TVT	0.573/100; 0.312/96; 0.264/48	18	8	0.053
6	Mixture 3	0.571/100; 0.310/75; 0.369/77	21	5	0.040
7	Sample 6 after TVT	0.312/100; 0.573/84; 0.370/42	19	12	0.035

*d*/*I* interplanar spacings (nm), reflexes intensity (%), *D* crystallite sizes, *C* concentration of acid groups

Table 2 presents also other physicochemical parameters of the VHP samples synthesized at 300 °C. The size of crystallites *D* calculated from the Debye–Scherrer equation is about 20 nm and only for the sample obtained in the presence of citric acid it is slightly larger. The specific surface area *S* is on the level of value *S* for initial oxides but it increases in two times after thermal vacuum treatment. General acidity *C* behaves inversely, i.e., *S* decreases. The order of its quantity corresponds to the data determined earlier for samples with analogous crystal structure prepared by means of other synthesis methods [42].

Another peculiarity of the solid–state interactions in the studied mixtures is formation of binary ammonium–vanadyl pyrophosphate phase (NH<sub>4</sub>)<sub>2</sub>[V(4+)O]<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> (AVPP) with the ratio *P*/*V* = 1.33. This substance is the precursor of oxidation ammonolysis catalysts and as a rule it is formed from vanadyl hydrophosphate in the presence of ammonia at 400 °C [13–15, 43]. In our case, separate reflections appear on diffractograms after treatment at 250 °C (for the system 2, *d* = 0.643, 0.375, 0.360, 0.306, 0.275 nm). However, it is predominant in the reaction products only at 400 °C (for system 1 in the presence of ammonia excess). Characteristic

feature of the structure AVPP is different ratio of peaks intensities on the diffractograms. Thus for the sample obtained in system 2, the most intensive is the reflection corresponding to *d* = 0.275 nm, in system 3, *d* = 0.375 nm, whereas literature data report that XRD pattern from plane with *d* = 0.565 nm is the most intensive [15]

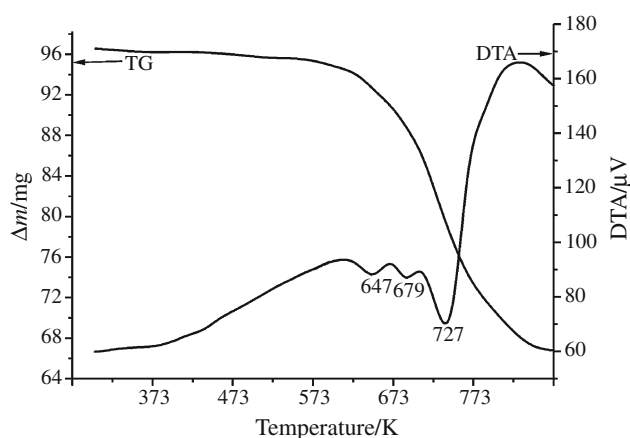
Figure 3 presents the characteristic curve of DTA-TG for the sample containing AVPP: endoeffects at 374 and 406 °C correspond to two NH<sub>3</sub>-molecules removal [38] and endoeffect at 454 °C connected with dehydration–oxidation of formed at first stage VHP phase according to scheme described in [27, 42].

## Conclusions

This article studies for the first time, the tendencies of solid-state reactions in the closed systems for both pure vanadium–phosphorus oxides and with the addition of reductants through control of gaseous phase composition. Thus, an alternative possibility of preparation of catalyst precursors for oxidation and ammooxidation of hydrocarbons—semihydrate of vanadyl hydrophosphate and mixed ammonium–vanadyl pyrophosphate is presented. They are characterized by specific surface areas and general acidity suitable for catalysts as well as crystals of nanosizes. However, for obtaining of pure phases VHP and AVPP using the presented method additional research is required.

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**Fig. 3** The curves of TG and DTA for phosphate (NH<sub>4</sub>)<sub>2</sub>(VO)<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>, obtained at 400 °C from vanadium dioxide and diammonium hydrophosphate

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