Basic crystallographic data and chemical character of the precursor of the vanadyl phosphate catalyst prepared in the medium of hydrochloric acid

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The analysis of infrared spectra and X-ray diffractograms of the precursor of the vanadyl phosphate catalyst prepared in the medium of concentrated hydrochloric acid has enabled us to come to the conclusion that this species is vanadyl hydrogen phosphate crystallizing in the rhombic system with lattice parameters $a = (9.71 \pm 0.02) \times 10^{-10}$ m, $b = (13.03 \pm 0.02) \times 10^{-10}$ m, and $c = (13.96 \pm 0.02) \times 10^{-10}$ m, the volume of unit cell being $V = 1766 \times 10^{-30}$ m³. The ratio n(P): n(V) = 1.1—1.2 is usually used for preparing the catalyst. Thus the precursor may generally be expressed as VOHPO₄·xH₂O·yH₃PO₄.

В результате изучения ИК-спектров и дифракционных рентгенограмм прекурсора ванадиево-фосфорного катализатора, полученного в среде концентрированной соляной кислоты, сделан вывод, что этим прекурсором является кислый фосфат ванадила, кристаллизующий в ромбической сингонии с параметрами решетки $a = (9,71 \pm \pm 0,02) \cdot 10^{-10}$ м, $b = (13,03 \pm 0,02) \cdot 10^{-10}$ м, $c = (13,96 \pm 0,02) \cdot 10^{-10}$ м и объемом $V = 1766 \cdot 10^{-30}$ м³. Для приготовления катализатора обычно выбирается соотношение n(P) : n(V) = 1,1-1,2. Таким образом, состав прекурсора можно в общем случае выразить, как VOHPO₄ · $xH_2O \cdot yH_3PO_4$.

The vanadyl phosphate catalysts used for partial oxidation of C_4 hydrocarbons to maleic anhydride are synthesized through an intermediary compound, *i.e.* precursor. The structure and chemical composition of this intermediate depend on the method of its preparation. The chemical composition of phases as well as the crystallographic characteristics and catalytic properties of multiphase active vanadyl phosphate catalyst [1-3] is governed by chemical character and crystal structure of the precursor. This fact stimulated us to investigate the precursor of the V-P-O and V-P-O-M (M is modifying cation) catalyst prepared in the medium of concentrated hydrochloric acid.

Experimental

All chemicals used in this study were anal. grade reagents. The precursor was prepared analogously as described in patent [4]. V_2O_5 was dissolved in concentrated HCl at raised temperature (for preparing the modified precursor a salt consisting of the modifying cation and a less stable nonoxidizing anion, *e.g.* FeCl₂·4H₂O was added into the solution, too) and allowed to react with calculated amount of H₃PO₄ by boiling under reflux for 2 h. Then the solution was poured into an open flask (2 dm³ flask cut at about two thirds) with spherical bottom placed in an electric flask heater. The solution was gradually evaporated up to dry in a fume cupboard (final temperature of drying 280 °C at most). The obtained green or bluish product is the precursor of the V—P—O or V—P—O—M catalyst. After dissolving the precursor in water, it was found that the content of phosphorus in the form of Mg₂P₂O₇ corresponded to the chosen ratio of n(P):n(V) and the content of vanadium(IV) in individual samples determined by titration with a standardized solution of KMnO₄ was greater than 99.1 %. The investigated precursors exhibited the ratios n(P):n(V) = 1.2 and n(M):n(V) = 0.14.

The X-ray diffractograms of the powdered samples put on a glass support covered with balsam were obtained with an instrument DRON 2 in the range of diffraction angles $\Theta = 6^{\circ}$ —26°. The X-ray radiation of a copper anode (voltage 26 kV, current 10 mA) and a nickel filter for eliminating the component of K_{β} radiation were used. The calibration of diffraction lines was performed by means of a silicium standard.

The infrared spectra were taken on an instrument Perkin—Elmer 577 in the region $\tilde{v} = 200-4000 \,\mathrm{cm}^{-1}$ by using the method of the KBr tablets containing the catalyst in the ratio 1:200.

Results and discussion

The precursor of the vanadyl phosphate catalyst prepared by the above method has not yet been characterized in literature. Its X-ray diffractogram presented in paper [5] lacks any detailed analysis. On the basis of diffractograms (Fig. 1), X-ray structural data (Table 1), and infrared spectra (Fig. 2) we characterized the precursor crystallographically as well as chemically.

The analysis of both the obtained diffractograms has shown that the diffraction indices may be assigned to individual lines in harmony with the equation

$$\sin^2 \Theta_{hkl} = 0.00630h^2 + 0.00350k^2 + 0.00305l^2 \tag{1}$$

where Θ_{hkl} is the corresponding diffraction angle. The validity of this type of equation gives evidence that the investigated precursor crystallizes in the rhombic system [6]. The determined coefficients in eqn (1) were used for calculating the lattice parameters of unit cell of the precursor: $a = (9.71 \pm 0.02) \times 10^{-10}$ m, $b = (13.03 \pm 0.02) \times 10^{-10}$ m, $c = (13.96 \pm 0.02) \times 10^{-10}$ m, and the volume of unit cell $V = 1766 \times 10^{-30}$ m³.



Fig. 1. X-Ray diffractograms of the precursors of vanadyl phosphate catalysts; n(P): n(V) = 1.2. a) Nonmodified sample; b) sample modified by iron, n(Fe): n(V) = 0.14.

Table	1
Table	1

Values of d_{hkl} and diffraction indices determined for the precursor VOHPO₄·0.3H₂O·0.2H₃PO₄

d_{hkl} From diffraction angles	d_{hkl} Calculated	Diffraction indices
6.941	6.923	002
6.540	6.515	020
6.160	6.119	012
5.683	5.668	102
4.524	4.550	210
4.125	4.144	031
3.986	3.992	113
3.673	3.688	032
3.587	3.571	023
3.364	3.371	014
3.278	3.284	104
3.163	3.174	041
3.089	3.089	140
2.930	2.933	124
2.832	2.834	204
2.789	2.791	005
2.652	2.655	241
2.600	2.603	313
2.392	2.392	401
2.232	2.229	324
2.040	2.041	154
1.899	1.901	335
1.852	1.852	512
1.834	1.832	405
1.765	1.764	246



Fig. 2. Infrared spectra of the precursors of vanadyl phosphate catalysts; n(P): n(V) = 1.2. 1. Nonmodified sample; 2. sample modified by iron, n(Fe): n(V) = 0.14.

The basis for clearing up the chemical composition of the precursor may be obtained by analysis of its infrared spectrum (Fig. 2). The character of the infrared spectra indicates that we are up against an inorganic phosphate containing the PO_4^{3-} ions [7, 8]. However, the spectrum of the precursor significantly differs from the spectra of α - and β -VOPO₄ [9]. In Fig. 2 we can see an intensive absorption band at $\tilde{v} = 1200 \,\mathrm{cm}^{-1}$ which is atypical of the above-mentioned phosphates. According to [7] a greater number of absorption bands in infrared spectrum and their shift to higher wavenumbers are characteristic of hydrogen phosphates. The investigated precursor exhibits a great deal of absorption bands in the region $\tilde{v} = 1000 - 1200 \,\mathrm{cm}^{-1}$ and under $700 \,\mathrm{cm}^{-1}$, which is in line with the mentioned generalization. The character of the infrared spectra points out a decrease in symmetry of the point group \mathcal{T}_d characteristic of the PO₄³⁻ ions [8, p. 106] as well as a splitting of the degenerated vibrations of bonds. These facts enabled us to come to the conclusion that the precursor is vanadyl hydrogen phosphate. The assignment of absorption bands is given in Table 2. A sample of the pure compound VOHPO₄·4H₂O (obtained later from Dr. G. Ladwig) dried in nonoxidizing atmosphere at about 250 °C gave the X-ray diffractogram and record of infrared spectra equal to those of the precursor of the V-P-O catalyst. This result confirmed our preceding conclusions.

The fact that the investigated precursor exhibits characteristic crystal structure of its own with lattice parameters different from those of vanadyl diphosphate [1, 2] and the analysis of the infrared spectra of this precursor made possible the conclusion that the precursor of the V—P—O and V—P—O—M catalyst prepared in the medium of concentrated hydrochloric acid was vanadyl hydrogen phosphate VOHPO₄·xH₂O·yH₃PO₄ crystallizing in the rhombic sys-

Table 2

$\tilde{v}/\mathrm{cm}^{-1}$	Type of vibration (in HPO_4^{2-})	
1200, 1135, 1105	$v_3(PO_4)$ ($v_d(PO)$)	
1045	$v_1(PO_4)$ ($v_s(PO)$)	
1000	?	
980	v(V==O)	
925	v(POH)	
680, 640, 530	$v_4(PO_4)$ ($\delta_d(OPO)$)	
480, 410	$v_2(PO_4)$ ($\delta_d(OPO)$)	
345	$v_4(VO_6)$ ($\delta(OVO)$)	

Assignment of absorption bands in IR spectrum of the precursor of vanadyl phosphate catalyst [7, 8, 10]

tem. For the described method of preparation of the precursor (final temperature of heating at about 250 °C) the amount of crystal water was from 0.3 to 1 molecule (determined from derivatogram). The content of H_3PO_4 is dependent on the ratio n(P): n(V). In our case we obtained 0.2 molecule per one molecule of hydrogen phosphate.

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