

X-RAY DIFFRACTOGRAMS AND IR SPECTRA OF MODIFIED VANADIUM-PHOSPHATE CATALYSTS

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Structure of vanadium-phosphate catalysts ($V : P = 1 : 1.2$) modified by addition of Li, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pd, Cd, Sn or Ce has been studied by X-ray diffractometry and IR spectroscopy. Dimension of particles is diminished, and degree of arrangement of structure of the contact catalyst is lowered in the presence of the additives as compared with the non-modified catalyst, which can be explained by incorporation of these additives (except for Pd) in the lattice of the basic catalyst. Crystalline phase $(VO)_2P_2O_7$ has been found in all the catalysts besides the cyclic anion $P_4O_{12}^{4-}$; the non-modified and the Ba-containing catalysts contain also the compound $VO(PO_3)_2$.

Our previous paper¹ gives some data on influence of addition of various ions ($M = Li, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pd, Sn$ or Ce) on catalytic properties of a $V-P-O$ catalyst ($V : P = 1 : 1.2$) used in oxidation of butane to maleic anhydride (MA) with air. For explanation of the obtained results it is necessary to have various pieces of information about the prepared contact catalysts which can be obtained by various physico-chemical methods. Such information involves first of all data about the chemical system being formed on interaction of the starting components during preparation of the catalysts.

There are not many reports dealing with formation of vanadium-phosphate catalysts²⁻⁶. G. Ladwig² studied in detail this process of formation of a catalyst ($V : P = 1 : 1$) for oxidation of butenes to MA. This catalyst was prepared by a method based on treatment of V_2O_5 with concentrated phosphoric acid. The author showed that under certain condition the starting catalyst having the composition of $\alpha-V^vOPO_4$ is transformed into vanadyl diphosphate $(VO)_2P_2O_7$, a crystalline substance with orthorhombic structure.

Nakamura and coworkers³ prepared a series of vanadium-phosphate catalysts with the $V : P$ ratio varying within the limits $1 : 0.09$ to $1 : 4$. Ammonium meta-vanadate and orthophosphoric acid were used as starting substances. The authors found by X-ray diffractometry the presence of an unknown phase in the catalyst of the ratio $V : P = 1 : 0.2$; the other samples with the ratios $V : P = 1 : 0.37$ to $1 : 4$ were X-ray amorphous.

Khulbe and Mann⁴ prepared V-P-O catalysts (V : P = 1 : 0.1 to 1 : 3) from ammonium metavanadate and ammonium dihydrogen phosphate. The authors found V₂O₅ with an unknown phase in the catalyst with the ratio V : P = 1 : 1; at the ratios V : P = 1 : 1.5 or 1 : 2 the prepared contact catalysts appeared as amorphous, and in the catalyst with V : P = 1 : 3 the authors found an unknown phase.

Using the method of ref.³ the communication⁵ describes preparation of a series of V-P-O catalysts with the ratios V : P = 1 : 0.55 to 1 : 3.24. The report gives composition of the catalysts prepared: those with the V : P ratios 1 : 0.91 and 1 : 1.14 consist of three phases - α -V^{VO}PO₄, V-P-O mica (R[(V^{VO}O)_{1-x}(V(IV)O)_xPO₄]_n·n H₂O) and traces or small amounts of (VO)₂P₂O₇; those with higher phosphorus content consist of β -VO(PO₃)₂ (V : P = 1 : 2.07), or of metaphosphate V(III)(PO₃)₃ (V : P = 1 : 3.24).

Bordes and Courtine⁶ also investigated structural and catalytic properties of the V-P-O system (V : P = 1 : 0.5 to 1 : 2) prepared from NH₄VO₃, V₂O₅, NH₄H₂PO₄ and H₃PO₄. The authors found the catalysts to consist of (VO)₂P₂O₇; in samples with V : P = 1 : 1.6 they identified the presence of VO(PO₃)₂ and V(III)(PO₃)₃.

Thus there are differences between the conclusions of various authors³⁻⁶ concerning composition of the catalysts prepared by nearly analogous methods. The mentioned reports²⁻⁶ give the data concerning vanadium-phosphate catalysts containing no additions of other ions. In literature there are no data on influence of other components on composition and structure of the basic catalyst. The aim of our investigation was (determined by this situation) application of X-ray diffractometry and IR spectroscopy to study of chemical systems formed in the process of preparation and catalytic testing of a vanadium-phosphate catalyst (V : P = 1 : 1.2) containing addition of various ions M (M = Li, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pd, Cd, Sn or Ce).

EXPERIMENTAL

The catalysts were prepared by two methods (*I* and *II*). The method *I* was based on interaction of H₃PO₄ with solution of V₂O₅ in HCl and addition of a defined amount of salt of the respective element with a non-oxidizing anion. After evaporation the dry residue was calcinated in air, treated with an inert gas and with a mixture of aliphatic hydrocarbon and air. The method *II* consisted in reaction of V₂O₅ with H₃PO₄ and salt of the respective element with a non-oxidizing anion and subsequent heating of the obtained substance in a stream of SO₂ up to 1 050 K.

The diffractograms of the samples were investigated, after their testing for catalytic activity, with the use of a DRON-2 apparatus equipped with an X-ray tube with copper anode (26 kV, 10 mA) and with a nickel filter to filter off K _{β} radiation. Indexing of the reflections present in the obtained diffractograms (Fig. 1a,b,c) was carried out on the basis of equation

$$\sin^2 \theta_{hkl} = 0.0099h^2 + 0.0065k^2 + 0.0020l^2$$

which corresponds to the orthorhombic system. Coefficients of the above equation were obtained and gradually defined with more precision by the method given in ref.⁷ taking into account the

data about parameters of the elementary cell^{2,6}. Assignment of reflections to this structure was considered possible, if the difference between the calculated and experimental values of $\sin^2 \theta$ did not exceed ± 0.0003 . All the other reflections which did not fulfil this condition were assigned by us to an unknown structure; these reflections are not denoted with indexes in the line diagrams of the catalysts. The parameters of elementary cell calculated from the obtained data are $a = 7.74 \cdot 10^{-10}$ m, $b = 9.55 \cdot 10^{-10}$ m, $c = 17.22 \cdot 10^{-10}$ m, $V = 1.2728 \cdot 10^{-30}$ m³.

Intensity of the reflections was evaluated visually according to their height. Fig. 1*a,b,c* gives relative heights of the reflections in the obtained diffractograms. As a basic reference reflection we chose the reflection with the index 200 in diffractograms of the unmodified catalysts (Fig. 1*a-1*; 1*c-1*); their height is the same in the both cases.

The IR spectra of the catalysts were measured (after testing the catalytic activity of the catalysts) with the use of a Perkin-Elmer 577 apparatus in the region 4 000 to 200 cm⁻¹. Samples were prepared by the method of KBr disc (1 : 200); mass of the disc was 0.25 g in all cases. As reference standards we used pure samples of (VO)₂P₂O₇, K₂[VOP₂O₇], VO(PO₃)₂ and V(III)(PO₃)₃ which we obtained as a present.

RESULTS AND DISCUSSION

X-Ray diffractometric investigation of the catalysts. Most diffractograms of the catalysts (Method I, Fig. 1*a,b*) only exhibit reflections which can be assigned to orthorhombic structure. In accordance with published data^{2,6} these reflections are characteristic of vanadyl diphosphate (VO)₂P₂O₇. Exceptional are the catalysts V-P-O-Pd (V : Pd = 1 : 0.2), V-P-O-Cd (V : Cd = 1 : 0.2) and V-P-O-Li (V : Li = 1 : 0.2 and 1 : 0.5) whose diffractograms also contain other reflections which cannot be assigned to orthorhombic structure (Fig. 1*a-2, 7*; 1*b-9, 10*). Diffractogram of the V-P-O-Pd catalyst (V : Pd = 1 : 0.2) contains two intensive reflections which can be assigned to palladium metal⁷. In the case of further three catalysts containing Cd or Li the origin of new reflections is not known. It is possible that during preparation of these catalysts the Cd or Li ions react partially with orthophosphoric acid to give certain phosphates.

The diffractograms of each catalyst prepared by us by the method II exhibit, besides the reflections due to (VO)₂P₂O₇, some extra reflections (Fig. 1*c*). It must be noted that intensity of these reflections increases with increasing phosphorus content in the unmodified catalysts (Fig. 1*c 1-5*). The authors^{5,6} came to a conclusion about the presence of VO(PO₃)₂ in the catalysts having the ratio V : P < 1; the data of ref.⁶ concerning distances between the planes in this substance are roughly the same as our results. From this data it is presumed that the reflections in diffractograms of the catalysts prepared by the method II which cannot be assigned to (VO)₂P₂O₇ are due to the mentioned metaphosphoric compound. An exception is the reflection at $2\theta = 41.6^\circ$ found in the diffractograms of the V-P-O-Cd catalysts prepared by both the methods I and II: this reflection obviously belongs to some compound of phosphorus and cadmium.

The obtained data indicate that intensity of reflections in the diffractograms of the catalysts prepared by the method I and containing admixtures of ions of other

elements is lower than intensity of the same reflections in the diffractograms of the unmodified catalyst (1a-1). This can be seen most distinctly when comparing the most intensive reflections with the indexes 200, 031 and 032, *i.e.* those which correspond to relatively small angles of reflection. As the conditions of preparation of the given catalysts and those of testing their catalytic activities were the same or analogous (temperature, time of testing), the observed lowering of intensity of reflections indicates first of all that, due to the presence of modifying admixtures, the dimension of particles and degree of arrangement of the catalyst structure are lowered^{8,9}. Such a phenomenon is usually characteristic of solid solution, where the presence of additional or substituent atoms or holes in the solvent lattice (in the given instance $(VO)_2P_2O_7$) results in changed intensity of reflections. In accordance with ref.⁸ this change is due first to changed amplitude of the structure, next to disorders in arrangement of atoms and local defects of lattice which result in a change of diffusion background and effective thermal factor.

The obtained results indicate that reflection intensity in the diffractograms of the catalysts with various added amounts of Co, Sn, Mn or Li ions decreases with increasing concentration of these admixtures (Fig. 1b 1-14). The catalysts modified by addition of Co, Sn or Mn show a certain relation between selectivity of formation of MA¹ and intensity of selected reflections: the lowest selectivity was observed with the catalysts which show the lowest intensity of the mentioned reflections. The Li-containing catalysts are exceptional in this respect: their diffractograms show decreasing intensity of reflections with increasing amount of the added Li, but the selectivity is only slightly changed.

We prepared only two catalysts by the method II with modification admixtures of Cd or Cu (one atom per 5 atoms of vanadium). Therefore, the conclusions which can be obtained from comparison of intensity of reflections in the diffractograms of the catalysts cannot be unambiguous. From Fig. 1c - 1, 6 and 7 it can be seen *e.g.* that intensity of reflections with the indexes 200, 031 and 032 in the diffractogram of the V-P-O-Cu catalyst is approximately the same as that in the diffractogram of the unmodified catalyst, and in the case of the V-P-O-Cd catalyst it is smaller. In spite of that it can be generally stated that intensity of reflections (*i.e.* dimension of particles and arrangement of the structure) of the catalysts containing copper and cadmium is higher, if the catalyst is prepared by the method II. It can be presumed that, to some extent, this difference in structure properties of the said catalyst is due to differences in temperature regime during their preparation and, especially, to the fact that the catalysts prepared by the method II were preheated to higher temperatures than those prepared according to the method I. Selectivity of oxidation of butane to MA with the catalysts containing Cu and Cd ions and prepared by the method II is substantially lower than that of the same catalysts prepared by the method I (ref.¹). Detailed investigation of influence of temperature treatment and of dimension of particles on catalytic activity of the contacts will necessitate further experiments.

Investigation of the catalysts by IR spectroscopy. Spectrum of the unmodified catalysts (Fig. 2a, 1; 2c, 3) shows the following absorption bands in the region $1\ 250$ to 700 cm^{-1} : $1\ 250$, $1\ 220$, $1\ 150$, $1\ 130$, $1\ 070$, 990 , 945 , 825 , 795 and 745 cm^{-1} and a series of bands in the region below 700 cm^{-1} . In the spectrum of the catalyst prepared by the method *II* further bands are seen at $1\ 340$ and $1\ 285\text{ cm}^{-1}$. On the basis of ref.¹⁰ the bands with wave numbers above 700 cm^{-1} can be assigned to valence vibrations of P-O bonds in various anions of phosphorus with oxygen, and the bands from the region below 700 cm^{-1} can be assigned to deformation vibrations of these groupings. Complicated shape of the individual absorptions (*e.g.*

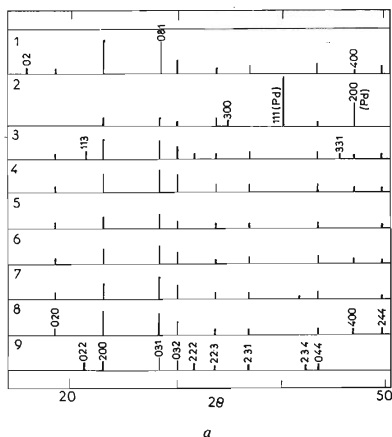
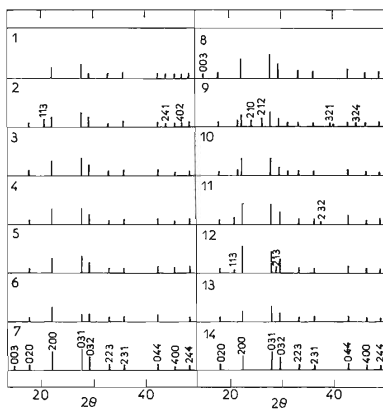
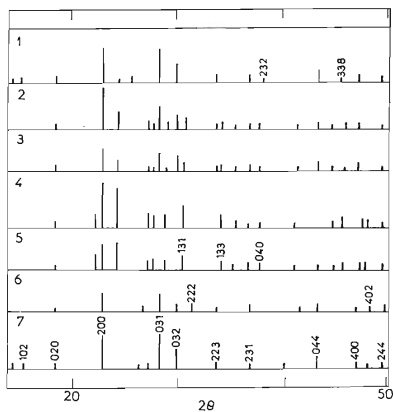
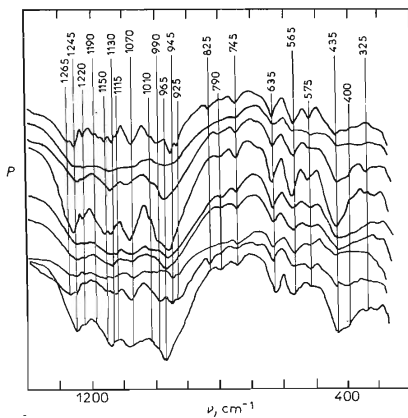


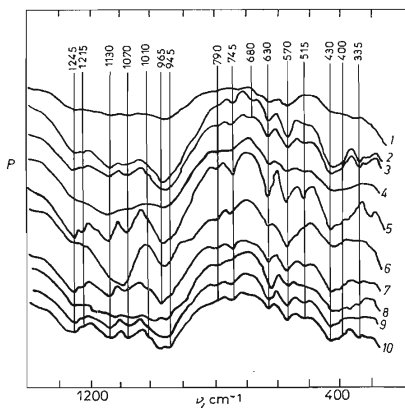
FIG. 1

X-ray diffractograms of the powdered catalysts. *a)* Method *I* (V : M = 1 : 0.2). 1. V-P-O, 2. V-P-O-Pd, 3. V-P-O-Zn, 4. V-P-O-Cu, 5. V-P-O-Fe, 6. V-P-O-Ni, 7. V-P-O-Cd, 8. V-P-O-Ba, 9. V-P-O-Ce, *b)* Method *I*. 1. V-P-O-Co (V : Co = 1 : 0.5), 2. V-P-O-Co (V : Co = 1 : 0.3), 3. V-P-O-Co (V : Co = 1 : 0.2), 4. V-P-O-Co (4 : Co = 1 : 0.1), 5. V-P-O-Co (V : Co = 1 : 0.05) 6. V-P-O-Sn (V : Sn = 1 : 0.2), 7. V-P-O-Sn (V : Sn = 1 : 0.1), 8. V-P-O-Sn (V : Sn = 1 : 0.05), 9. V-P-O-Li (V : Li = 1 : 0.5), 10. V-P-O-Li (V : Li = 1 : 0.2), 11. V-P-O-Li (V : Li = 1 : 0.1), 12. V-P-O-Li (V : Li = 1 : 0.05), 13. V-P-O-Mn (V : Mn = 1 : 0.5), 14. V-P-O-Mn (V : Mn = 1 : 0.2), *c)* Method *II*. 1. V-P-O (V : P = 1 : 1.19), 2. V-P-O (V : P = 1 : 1.27), 3. V-P-O (V : P = 1 : 1.33), 4. V-P-O (V : P = 1 : 1.65), 5. V-P-O (V : P = 1 : 1.78), 6. V-P-O-Cd (V : Cd = 1 : 0.2), 7. V-P-O-Cu (V : Cu = 1 : 0.2)

*b**c*



a



b

in the intervals 1 265–1 220, 1 190–1 115, 990–925 cm^{-1}) can be explained by transfer of degeneration which is characteristic of crystalline state of substances. More detailed assignment of the observed bands is given in Table I.

To explain the effect of admixtures of various elements on structural properties of the V-P-O catalysts, it is necessary to find the differences between the spectra of the modified and unmodified catalysts. Comparison of the respective data indicates that the spectra of the unmodified catalysts are usually more complex than those of the V-P-O-M catalysts. The latter lack the individual little intensive maxima and breaks of the basic bands, which is characteristic of the unmodified catalysts. This can be explained by decreased degree of structural order. Generally it must be noted that the spectra of the modified catalysts do not contain any extra bands

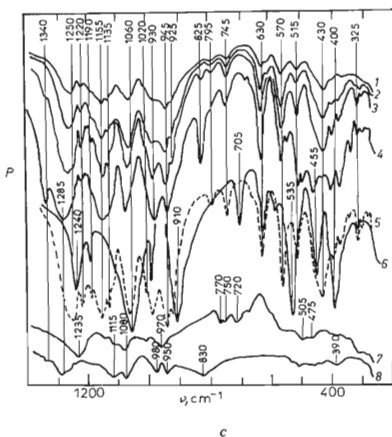


FIG. 2

IR spectra of vanadium-phosphate catalysts. *a*) Method I (V : M = 1 : 0.2) 1. V-P-O, 2. V-P-O-Pd, 3. V-P-O-Zn, 4. V-P-O-Cu, 5. V-P-O-Fe, 6. V-P-O-Ni, 7. V-P-O-Cd, 8. V-P-O-Ba, 9. V-P-O-Ce, the numbers of curves from the top are 1–9, *b*) Method I, 1. V-P-O-Co (V : Co = 1 : 0.5), 2. V-P-O-Co (V : Co = 1 : 0.3), 3. V-P-O-Co (V : Co = 1 : 0.2), 4. V-P-O-Sn (V : Sn = 1 : 0.2), 5. V-P-O-Sn (V : Sn = 1 : 0.1), 6. V-P-O-Mn (V : Mn = 1 : 0.5), 7. V-P-O-Mn (V : Mn = 1 : 0.2), 8. V-P-O-Li (V : Li = 1 : 0.5), 9. V-P-O-Li (V : Li = 1 : 0.2), 10. V-P-O-Li (V : Li = 1 : 0.05), *c*) 1. V-P-O-Cu (method II, V : Cu = 1 : 0.2), 2. V-P-O-Cd (method II, V : Cd = 1 : 0.2), 3. V-P-O (method II, V : P = 1 : 1.19), 4. V-P-O (method II, V : P = 1 : 1.27), 5. $(\text{VO})_2\text{P}_2\text{O}_7$, 6. $\text{K}_2[\text{VOP}_2\text{O}_7]$ 7. $\text{V}(\text{III})(\text{PO}_3)_3$, 8. $\text{VO}(\text{PO}_3)_2$

as compared with the spectra of the unmodified catalysts. Individual bands in spectra of the modified catalysts are shifted by 5 to 20 cm^{-1} , which can be explained by changed dimension of particles and effect of admixtures on bond relations.

Comparison of intensities of bands in the region 1 250 to 700 cm^{-1} reveals an increase in absorption of spectra of most modified catalysts as compared with the unmodified ones. Exceptions are the catalysts V-P-O-Co (V : Co = 1 : 0.5), V-P-O-Pd (V : Pd = 1 : 0.2), V-P-O-Cd (V : Cd = 1 : 0.2), V-P-O-Ba (V : Ba = 1 : 0.2), V-P-O-Li (V : Li = 1 : 0.2 and 1 : 0.05). As the absorption background was nearly the same, and concentration of the catalysts in KBr discs as well as procedure of their preparation were the same, too, the observed changes in intensities of absorption bands can be explained by a change of dipole moment of P-O bonds in the modified catalysts. In our opinion, the admixtures occupy the cavities formed by the components of the basic catalyst during formation of the modified catalysts. The incorporation of particles of the admixtures changes, at the same time, distribution of electron density in the anions. This fact causes polarity changes in the corresponding bonds, which results in intensity changes of absorption and probably also in the observed shift of maxima of the individual bands.

IR spectra of the unmodified catalysts were studied^{3,6}, and the results published agree with ours. The authors³ consider the bands in the regions 1 060–1 000, 1 170 to 1 060, 1 250–1 085 and 1 300–1 265 cm^{-1} to belong to the corresponding vibra-

TABLE I
Assignment of IR absorption bands of V-P-O and V-P-O-M catalysts (cm^{-1})

Wave number	Vibration	Anion
1 265, 1 250, 1 220	$\nu_{\text{as}}\text{O}-\text{PO}^-$	cycl. $\text{P}_4\text{O}_{12}^{4-}$
1 190, 1 155, 1 130	$\nu_{\text{s}}\text{O}-\text{PO}^-$	cycl. $\text{P}_4\text{O}_{12}^{4-}$
	$\nu_{\text{as}}\text{PO}_3$	$\text{P}_2\text{O}_7^{4-}$
1 080–1 060	$\nu_{\text{s}}\text{PO}_3$	$\text{P}_2\text{O}_7^{4-}$
1 010	$\nu\text{V}=\text{O}$	
990, 945, 925	$\nu_{\text{as}}\text{POP}$	$\text{P}_2\text{O}_7^{4-}$ cycl. $\text{P}_4\text{O}_{12}^{4-}$
1 340, 1 285	$\nu_{\text{as}}\text{O}-\text{PO}^-$	PO_3^-
825	$\nu_{\text{as}}\text{POP}$	PO_3^-
745	$\nu_{\text{s}}\text{POP}$	$\text{P}_2\text{O}_7^{4-}$
795, 745, 680		cycl. $\text{P}_4\text{O}_{12}^{4-}$
< 700	deformation vibration	

tions of *ortho*-, pyro-, tri- and higher linear phosphate ions. The authors⁶ assign the absorption bands in the region $1\ 265-1\ 125\text{ cm}^{-1}$ of spectrum of $(\text{VO})_2\text{P}_2\text{O}_7$ (overall 7 bands) to vibration of two PO_3 groups $\nu_{\text{as}}(\text{PO}_3)$ which differ by the type of symmetry, the bands at $1\ 055$, 980 , $935-920$ and 740 cm^{-1} being assigned to the vibrations $\nu_s(\text{PO})_3$, $\nu\text{V}=\text{O}$, $\nu_{\text{as}}(\text{POP})$ and $\nu_s(\text{POP})$, respectively.

A survey of absorption spectra of various phosphate anions is given in the monograph¹⁰ in which the authors compare the calculated and experimental wave numbers for the anions $\text{P}_2\text{O}_7^{4-}$, $\text{P}_3\text{O}_9^{3-}$, $\text{P}_4\text{O}_{12}^{4-}$ and the chain anion $((\text{PO}_3)_2)_\infty$. From these data it follows that the anions $\text{P}_2\text{O}_7^{4-}$ have their band of the highest wave number at about $1\ 150\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{PO}_3)$), the cyclic anion $\text{P}_3\text{O}_9^{3-}$ and the chain anion $((\text{PO}_3)_2)_\infty$ about $1\ 300\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{O}-\text{PO}^-)$), and the cyclic anion $\text{P}_4\text{O}_{12}^{4-}$ about $1\ 285-1\ 235\text{ cm}^{-1}$ ($\nu_{\text{as}}(\text{O}-\text{PO}^-)$). The authors also give additional criteria for evaluation of the form of the anion $\text{P}_4\text{O}_{12}^{4-}$ which can be present in various conformations. *E.g.* it was found that occurrence of a band about 800 cm^{-1} along with another one between 750 and 700 cm^{-1} is characteristic of a conformation of S_4 symmetry, whereas conformation of C_{2h} (and also C_i) symmetry is characterized by two bands in the region of $\nu_s(\text{POP})$ wave numbers, *viz.* one at about 740 cm^{-1} and the other below 700 cm^{-1} . It is noted, that wave numbers of absorption bands of the other vibrations in various anions ($\nu_s(\text{O}-\text{PO}^-)$, ν_{as} and $\nu_s(\text{POP})$) have often very close values and, therefore, it is difficult to assign the observed bands unambiguously. It is also noteworthy that the authors^{3,4,6} are of the same opinion in that the absorption about $1\ 000\text{ cm}^{-1}$ is due to valence vibration of $\text{V}=\text{O}$ bond in the catalysts.

Taking into account literature data and absorption spectra of some compounds given in Fig. 2c, 5-8, we give interpretation of the absorption bands in Table I.

In accordance with such assignment and with respect to the fact that spectrum of each catalyst exhibits absorption bands about $1\ 250$, $1\ 150-1\ 130$ and $1\ 070\text{ cm}^{-1}$ it is concluded that the anions $\text{P}_2\text{O}_7^{4-}$ and cyclic $\text{P}_4\text{O}_{12}^{4-}$ are present in the contact catalysts. Except for spectra of the catalysts containing Pd and Cd (Method I), spectra of all the contact catalysts exhibit absorption bands at 790 and 745 cm^{-1} which are characteristic of S_4 symmetry of $\text{P}_4\text{O}_{12}^{4-}$ anion (so called "chess conformation"¹⁰), and some spectra of V-P-O-Co (V : Co = 1 : 0.3 and 1 : 0.2), V-P-O-Cu (V : Cu = 1 : 0.2) and V-P-O-Ba (V : Ba = 1 : 0.2) exhibit a band at 680 cm^{-1} which can be assigned to the $\text{P}_4\text{O}_{12}^{4-}$ ion with C_{2h} symmetry (chair conformation). As intensity of this band is small, occurrence of the corresponding anion cannot be excluded in the other catalysts, too. The fact that the diffractograms of the modified catalysts contain practically only the reflections due to $(\text{VO})_2\text{P}_2\text{O}_7$, whereas the IR spectra exhibit the bands which can be (in our opinion) assigned to vibrations of two various anions ($\text{P}_2\text{O}_7^{4-}$ and $\text{P}_4\text{O}_{12}^{4-}$), can be explained either by the part of the catalytic substance with $\text{P}_4\text{O}_{12}^{4-}$ anions being present in an X-ray amorphous state or by close lattice type and parameters of the given cyclic vanadyl phosphate and $(\text{VO})_2\text{P}_2\text{O}_7$.

Besides these two anions, in the spectrum of the unmodified catalysts and also V-P-O-Ba catalyst there are bands corresponding to vibrations of (PO_3) anion in metaphosphate compound $\text{VO}(\text{PO}_3)_2$ (1 340 and 825 cm^{-1}).

The absorption band with wave number about 1 010 cm^{-1} which we assign to the V=O bond vibration makes itself felt as a break in spectra of most catalysts. Exceptions are the catalysts containing admixtures of Pd, Ni, Ba, Sn (V : M = 1 : 0.2) and Co (V : Co = 1 : 0.5 and 1 : 0.3) or Mn (V : Mn = 1 : 0.5), *i.e.* the catalysts which show an extremely low selectivity for MA. It is supposed that in spectra of these catalysts the absorption band of V=O bond is shifted towards lower wave numbers and is overlapped by a more intensive band of $\nu_{\text{as}}(\text{POP})$ vibration (about 965 cm^{-1}).

Difference between conclusions of our investigations and those of refs^{2,6} concerning composition and structure of the vanadium-phosphate catalyst in which the ratio V : P is equal or close to 1 consists practically only in interpretation of the absorption bands at 1 265, 1 250 and 1 220 cm^{-1} . As it can be seen in Table I we assign these bands to vibration of the anion $\text{P}_4\text{O}_{12}^{4-}$ in the catalyst, whereas *e.g.* the authors⁶ assign them to vibration of the group $\nu_{\text{as}}(\text{PO}_3)$ in $(\text{VO})_2\text{P}_2\text{O}_7$. This problem will necessitate further explanation. If the mentioned difference is not taken into account, we can state a good agreement between our conclusions and those of refs^{2,6}, and in accordance therewith the vanadium-phosphate catalyst with the ratio V : P about 1 : 1 is composed substantially of crystalline $(\text{VO})_2\text{P}_2\text{O}_7$.

The samples of $(\text{VO})_2\text{P}_2\text{O}_7$, $\text{K}_2[\text{VOP}_2\text{O}_7]$, $\text{VO}(\text{PO}_3)_2$ and $\text{V}(\text{III})-(\text{PO}_3)_3$ were kindly supplied for our studies within the framework of international scientific agreement between Central Institute of Inorganic Chemistry, Academy of Sciences Berlin (G. Ladwig), Central Institute of Organic Chemistry, Academy of Sciences Berlin (H. Seeboth and coworkers) and our University.

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