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Synthesis of Multicomponent Oxide Low-Dimensional Systems on the Surface of Porous Silicon Dioxide Using the Molecular Layering Method

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Abstract—Reflecting the research in the field of the surface chemistry of solids over the last 25–30 years, the results related to the application of the molecular layering method for the synthesis of surface low-dimensional structures of complex composition are presented. The regularities of formation of multicomponent mono- and multilayers on the surface of solid-phase matrices are studied on examples of chemical interactions, by a preset program, of chlorides and oxychlorides of titanium, vanadium, phosphorus, chromium, zinc, and iron with hydroxy and secondary functional groups of porous silicon dioxide. On the basis of chemical-analytical and spectroscopic data, structural schemes of synthesized products are proposed and functional interactions in multicomponent monolayers on the surface are considered. The reactivity of the element chlorides and oxychlorides as a function of the chemical composition of surface functional groups of silica and on synthesis conditions is estimated. In view of the revealed regularities of formation of complex low-dimensional systems on silica surface, prospects of application of the resulting data are considered for elaboration of scientific foundations of the chemical nanotechnology of production of solid-phase materials of various functional use, based on the molecular layering method.

During the last 25–30 years, investigations into the chemistry and technology of the surface of solid substances and materials have been actively developed [1–12], scientific foundations of chemical-informational synthesis have been formed [13, 14], and thermodynamic notions as applied to new processes and systems have been formulated [15, 16]. The development of high technologies, including the ways of synthesis of low-dimensional systems (nanotechnology), can not be imagined without achievements in the field of precise inorganic and organic synthesis.

In the present time, promising directions of solid-phase material science are primarily related to creation of low-dimensional structures. Traditional physical processes in vacuum technology (vaporization, cathode sputtering) have exhausted their potential in terms of both precision and properties of target products. Increasing attention is paid to chemical approaches to elaboration of nanotechnology, which largely makes realizable synthesis of nanostructures on the solid-phase matrix surface. Among existing chemical precise methods of synthesis, one can point out the sol–gel technology, preparing Langmuir–Blodgett films, some variants of chemical vapor deposition, etc. One of the promising directions of development of nanotechnology is the synthesis of low-dimensional systems on the solid-phase matrix surface by the molecular layering method. The principles of the method have been formulated by Aleskovskii and Kol’tsov in the sixties. Experimental data on preparing oxide, nitride, sulfide, and carbon mono- and multilayers on the surface of various solid-phase matrices, estimation of promising fields of application of the new technology, and its technique are widely presented in the literature [3, 12–14, 17–28].

As is known, the synthesis of low-dimension systems on the surface of a solid matrix by the molecular layering method is realized by subsequent multiply repeated chemical reactions between surface functional groups (initial ones or newly formed in the preceding cycle of layering) and outside reagents in an inert gaseous or liquid medium. For complete substitution of reactive and accessible surface groups, the synthesis is carried out under conditions maximally far from equilibrium. It is possible to create artificial surface structures practically of any composition and structure by varying the chemical nature of active centers and the composition of reagents and the order of their feeding to the reactor on various stages of synthesis.

The goal of this review is to represent main

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Table 1. Chemical composition of silicas with TV, TCr, POHV, CrOHV, and CrOHT two-component oxide layers

First treatment	Sample notation	Second treatment	Sample notation	Content, $mmol/g_0$				
				Ti(IV)	Cr(VI)	Cr(III)	V(V)	P(V)
$TiCl_4$, H_2O	T	–	–	1.09	–	–	–	–
$TiCl_4$, H_2O	T	$VOCl_3$, H_2O	TV	1.09	–	–	0.90	–
$TiCl_4$, H_2O	T	CrO_2Cl_2, H_2O	TCr	1.09	1.09	–	–	–
PCl_3, Cl_2, H_2O	POH	–	–	–	–	–	–	0.96
PCl_3, Cl_2, H_2O	POH	$VOCl_3$, H_2O	POHV	–	–	–	1.07	0.96
CrO_2Cl_2, H_2	CrOH	–	–	–	–	1.04	–	–
CrO_2Cl_2, H_2	CrOH	$VOCl_3$, H_2O	CrOHV	–	–	1.03	1.15	–
CrO_2Cl_2, H_2	CrOH	$TiCl_4$, H_2O	CrOHT	1.26	–	1.03	–	–

achievements of the solid-surface chemistry over the last 25–30 years in the field of directed synthesis, by the molecular layering method, of multicomponent low-dimensional systems by examples of silica as matrix and vapors of certain Group III–VI chlorides or oxychlorides as reagents.

As main investigation objects we chose silica samples containing the surface groups $\equiv Si–OH$, $(\equiv Si–O–)_3TiOH$, $(\equiv Si–O–)_3P$, $(\equiv Si–O–)_3P(OH)_2$, $(\equiv Si–O–)_3VO$, $(\equiv Si–O–)_2CrO_2$, $(\equiv Si–O–)_2CrOH$, etc., which were treated, by a preset program, with the low-molecular reagents $TiCl_4$, PCl_3, $VOCl_3$, CrO_2Cl_2, etc.

For finding the structure of surface groups and obtaining true ratios, the composition of all the synthesized samples was recalculated and is given in this article per 1 g of anhydrous silica (g_0) whose amount (mg) in the samples was determined using the formula

$$[SiO_2] = 1000 - \{E_1(M_{E_1} + K_1/n_1\, M_O) + E_2(M_{E_2} + K_2/n_2\, M_O) + [OH]\, 1/2 M_{H_2O}\},$$

where E_1 and E_2 are the element contents (mmol/g); [OH] is the content of OH groups (mmol/g); M_{E_1}, M_{E_2}, M_0, and M_{H_2O} are the atomic and molecular weights of elements, oxygen, and water, respectively; and K_1/n_1, K_2/n_2, and 1/2 are the stoichiometric coefficients of oxides $[E_1]_{n_1}O_{K_1}$, $[E_2]_{n_2}O_{K_2}$, and H_2O, respectively.

SYNTHESIS OF ZONED COATINGS ON SILICA

Zoned oxide nanostructures on silica were prepared using the chlorides and oxychlorides $TiCl_4$, PCl_3, $POCl_3$, $VOCl_3$, and CrO_2Cl_2. The molecular layering method allows chemical assembling on a solid matrix surface of a multilayer structure with alternate monolayers of a specified chemical nature. The starting silicas with monolayers of $(\equiv Si–O–)_3TiOH$ (sample T), $(\equiv Si–O–)_3P(OH)_2$ (sample POH), and $(\equiv Si–O–)_2CrOH$ (sample CrOH) groups were treated with chlorides or oxychlorides [29, 30]. The chemical composition of the resulting products is represented in Table 1.

Reactions giving samples with layers alternating due to interaction of different element halides with hydroxy groups on silicon dioxide surface can be represented by the general scheme

$$(\equiv Si–O–)_nE_1(OH)_m + E_2O_kCl_l \longrightarrow [(\equiv Si–O–)_nE_1O–]_{m-p}E_2O_kCl_{l-p} + pHCl. \quad (1)$$

Here we observe a known condensation reaction. In the synthesis of an *i*th layer of another chemical nature, a halide reacts, for example, with hydroxy or other functional groups of the preceding monolayer. By this scheme, the author and co-workers synthesized two-zone oxide structures including iron, zinc, and titanium on reinforcing silica and silicon and titanium on alumina [31, 32].

The synthesis of two-component oxide layers on silica gel surface with use of redox reactions was first performed in [29, 30, 33–35]. The $(\equiv Si–O–)_3VO$ and $(\equiv Si–O–)_2CrO_2$ groups formed on silica gel surface by its treatment with vapors of the corresponding chlo rides possess strong oxidative properties. By treatment of such products with compounds possessing sufficiently strong reductive properties, such as phosphorus trichloride, one can effect addition of a new monolayer by means of a redox reaction between surface functional groups and the gaseous reagent [33, 35]. If, the reverse, there are strong reductive surface groups, such as $(\equiv Si–O–)_3P$, addition of a new monolayer can be effected by treatment of the surface with an oxidant containing a necessary element, for example, with vanadium oxychloride [30, 34].

Reactions of $(\equiv Si–O–)_3VO$ groups with PCl_3 and of

Table 2. Chemical composition of VP and PV products

Sample	Content per 1 g_0							
	P, mmol		V, mmol		$[OH]_{exp}$, mmol	$[OH]_{calc}$, mmol	P/V	$[OH]_{calc}/[OH]_{exp}$
	P^{3+}	P^{5+}	V^{5+}	V^{3+}				
Vanadium-containing silica gel	–	–	1.10	–	0.27	–	–	–
VP product	–	1.24	–	1.10	2.75	2.61	1.13	0.95
Phosphorus-containing silica gel	0.94	–	–	–	0.75	–	–	–
PV product	–	–	–	1.0	2.47	2.56	0.98	1.04

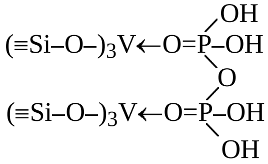
$(\equiv Si–O–)_3P$ groups with $VOCl_3$ allowed preparation on silica gel surface of two-component oxide layers of an almost the same composition but with different mutual location of phosphorus and vanadium hydroxide monolayers [30, 34]. Treatment of experimental data gave us grounds to propose that the reactions occur by a redox mechanism [schemes (2) and (3)] with *dπ–pπ* bond formation

$$(\equiv Si–O–)_3VO + PCl_3 \longrightarrow (\equiv Si–O–)_3V\longleftarrow OPCl_3, \quad (2)$$

$$(\equiv Si–O–)_3P + VOCl_3 \longrightarrow (\equiv Si–O–)_3PO\longleftarrow VCl_3. \quad (3)$$

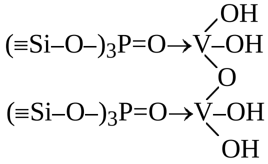
Further the composition and structure of the products formed by schemes (2) and (3) were studied in detail in [53].

Vapor-phase hydrolysis of the chlorine-containing samples obtained by schemes (2) and (3) leads to substitution of Cl by OH, followed by partial condensation. Apparently, VP and PV products are formed respectively by the schemes



$$\begin{array}{l} (\equiv Si–O–)_3V\leftarrow O{=}P(OH)(OH)– \\ \qquad\qquad\qquad\qquad\;\; O \\ (\equiv Si–O–)_3V\leftarrow O{=}P(OH)(OH)– \end{array} \quad (4)$$

VP sample

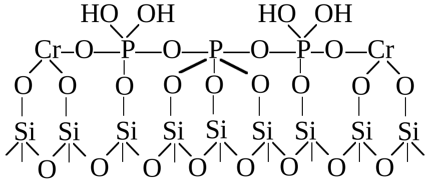


$$\begin{array}{l} (\equiv Si–O–)_3P{=}O\rightarrow V(OH)(OH)– \\ \qquad\qquad\qquad\qquad\;\; O \\ (\equiv Si–O–)_3P{=}O\rightarrow V(OH)(OH)– \end{array} \quad (5)$$

PV sample

The chemical composition of the samples is given in Table 2 and is in a good agreement with experi mental data. The slight deviation of the P/V ratio from unity [according to schemes (2) and (3)] is explained by partial reaction of $VOCl_3$ (~7% of the total content of V) or PCl_3 (~11% of the total content of P) with residual hydroxyls of silica gel.

Treatment of chromium(VI)-containing silica gel with PCl_3 vapors leads to redox reaction between $(\equiv Si–O–)_2CrO_2$ groups and PCl_3 with Cr–O–P bond formation. Together with this, addition of PCl_3 to the surface also occurs due to Si–O–P bonds [50]. The chemical composition of the hydrolyzed and dried product CrP is as follows (mmol/g_0): Cr(III) 0.82, P(V) 1.00, and OH 1.70, which is consistent with the structure



(6)

Multiple alternate treatment of silica gel with CrO_2Cl_2, PCl_3, and H_2O vapors results in a regular growth of the chromium and phosphorus contents of the samples (Table 3) [35].

Analysis of experimental data suggests the following mechanism of PCl_3 reaction with the Cr(VI)-containing sample. In the first stage, a redox reaction between PCl_3 and Cr(VI)-containing groups takes place, resulting in formation of $POCl_3$ and Cr(III)–oxygen groups, together with the possible partial addition of phosphorus to the surface. Phosphorus oxychloride can react with surface OH groups, and completeness of this reaction depends on the reactivity of $POCl_3$ under synthesis conditions. It is known that the amount and composition of phosphorus-containing groups formed by $POCl_3$ reaction with silica gel OH groups depend considerably on the concentration of the oxychloride which proved to be less reactive in the above processes than PCl_3, $VOCl_3$, $TiCl_4$, and other chlorides. It can be assumed that the phosphorus oxychloride formed by the redox reaction between Cr(VI)-containing groups and PCl_3 partially react with

Table 3. Chemical composition of products of multiple alternate treatment of silica gel with CrO_2Cl_2, PCl_3, and H_2O

Sample	Content, mmol/g_0				ΔCr_0	ΔP
	Cr(VI)	Cr(III)	Cr_0	P(V)		
Cr	0.98	0.05	1.03	0	1.03	0
CrP	0	0.82	0.82	1.00	–	1.00
CrPCr	1.11	1.03	2.14	1.00	1.32	–
$(CrP)_2$	0.21	1.83	2.04	1.73	–	0.73
$(CrP)_2Cr$	0.92	2.22	3.14	1.72	1.10	–

surface OH groups and is partially removed from the reaction zone. The latter process is favored by reaction conditions: The temperature of the reaction zone (180°C) is higher than the boiling point of $POCl_3$ (105°C), and the flow-type system allows continuous removal, by means of carrier gas, of gaseous products from the reaction zone.

In conclusion of this section we note that the first syntheses of two-zone phosphorus–titanium oxide structures on silica surface by combined condensation and redox reactions were performed in [3, 12]. All possible combinations (sixteen all in all) of titanium and phosphorus oxide monolayers (a total of four) were therewith obtained, and the physicochemical properties of the synthesized structures were studied.

WAYS OF FORMATION OF MULTICOMPONENT NONOLAYERS ON SILICA. STUDY OF THEIR STRUCTURE AND FUNCTIONAL NTERACTIONS ON THE SURFACE

Using the molecular layering method and experimental data on the stability of the Si–O–E bond under the action of hydrogen chloride, multicomponent element oxide monolayers can be synthesized in three ways: (a) by successive treatment silica with halides of elements E_1, E_2, E_3, etc.; therewith, compounds with E_2 and E_3 react with the OH groups not reacted with compounds with E_1 and E_2, respectively; (b) by substitution of E_1-containing surface groups by E_2-containing (the energy of the E_1–O bond is higher than that of E_2–O); therewith, E_1 halide evolves in the gas phase; and (c) by treatment of silica with a mixture of E_1 and E_2 halides. Let us consider the proposed synthesis variants in more detail.

a. Successive Substitution of Proton in Surface Silanols by Reactions with Various Element Halides.

Treatment of silica with phosphorus oxychloride gave P-containing silicas, the amount of OH groups in which decreased from 3.62 to 1.42 mmol/g_0 as their P content increased from 0 to 0.95 mmol/g_0. The resulting P silicas were treated with titanium or vanadium chlorides [36, 37]. In parallel with the above change of the P content, the amount of titanium- and vanadium-containing groups added due to reaction with silanol groups, decreased from 1.08 to 0.35 mmol/g_0 (Ti, Table 4) and from 1.11 to 0.31 mmol/g_0 (V, Table 5).

On the basis of chemical analysis data (P, Ti, V, and Cl) we calculated the content of various functional groups, as well as the amount of OH groups of the P silica, reacted with chlorides. The hydroxyl substitution degree α defined as the ratio of reacted OH groups to their number in the initial P silica decreases with increasing phosphorus content (decreasing hydroxyl concentration) of the P silica. The α value changes from 0.78 to 0.39 for PTi silicas and from 0.8 to 0.38 for PV silicas [36, 37]. A similar dependence was observed in reactions of halides (for example, $TiCl_4$) with a thermally dehydroxylated silica gel. However, the α value for the latter is higher than for P silicas with the same concentration of silanol groups (0.78 vs. 0.56). This indicates that the

Table 4. Chemical composition of PTi silicas (duration of treatment with $TiCl_4$ 30 min)

Content of initial P silicas, mmol/g_0						Content of PTi silicas, mmol/g_0									
P	Cl	Cl/P	≡PO	=POCl	OH	P	Ti	P/Ti	Cl	ΔCl	ΔCl/Ti	≡TiCl	$=TiCl_2$	$–TiCl_3$	OH
1.21	–	–	–	–	3.62	–	1.08	–	1.52	1.52	1.41	0.64	0.44	–	0.82
0.13	–	–	0.13	–	3.23	0.13	0.97	0.13	1.58	1.58	1.63	0.36	0.61	–	0.93
0.20	0.02	0.10	0.18	0.02	3.04	0.20	0.89	0.22	1.53	1.51	1.70	0.27	0.62	–	0.99
0.34	0.08	0.22	0.26	0.08	2.67	0.34	0.74	0.46	1.55	1.47	1.99	0.01	0.73	–	1.18
0.45	0.14	0.32	0.31	0.14	2.41	0.45	0.63	0.72	1.46	1.32	2.10	–	0.57	0.06	1.21
0.61	0.30	0.49	0.31	0.30	2.08	0.61	0.47	1.30	1.36	1.06	2.26	–	0.35	0.12	1.25
0.95	0.65	0.68	0.30	0.65	1.42	0.95	0.35	2.71	1.49	0.84	2.40	–	0.21	0.14	0.86

Table 5. Chemical composition of PV silicas (duration of treatment with $VOCl_3$ 30 min)

Content of initial P silicas, mmol/g_0						Content of PV silicas, mmol/g_0									
P	Cl	Cl/P	=PO	=POCl	OH	P	V	P/V	Cl	ΔCl	ΔCl/V	≡VO	=VOCl	$–VOCl_2$	OH
–	–	–	–	–	3.62	–	1.11	–	0.42	0.42	0.38	0.69	0.42	–	0.71
0.08	–	–	0.08	–	3.32	0.08	1.02	0.08	0.46	0.46	0.45	0.56	0.46	–	0.78
0.28	0.05	0.18	0.23	0.05	2.83	0.28	0.83	0.34	0.55	0.50	0.60	0.33	0.50	–	0.84
0.37	0.10	0.27	0.27	0.10	2.61	0.37	0.73	0.51	0.76	0.66	0.91	0.07	0.66	–	1.08
0.69	0.37	0.54	0.32	0.37	1.92	0.69	0.42	1.64	0.77	0.40	0.95	0.02	0.40	–	1.06
0.81	0.51	0.63	0.30	0.51	1.70	0.81	0.34	2.38	0.89	0.38	1.12	–	0.30	0.04	1.06
0.92	0.62	0.67	0.30	0.62	1.48	0.92	0.31	2.96	0.98	0.36	1.16	–	0.26	0.05	1.06

two silicas have different hydroxyl covers: Phosphorus-containing groups on the P silica surface, as well as newly synthesized titanium- and vanadium-containing groups, can shield part of OH groups. The effective «landing grounds» of $POCl_3$, $VOCl_3$, and $TiCl_4$ on the silica surface were calculated: w^{POCl_3} = w^{VOCl_3} = 0.314 nm^2 and w^{TiCl_4} = 0.351 nm^2 [38].

From the concentration of silica gel hydroxyls and their amount reacted with chlorides, Zolotavin and Levashova [59] calculated the number of hydroxyls shielded by one functional group: 0.7 for =POCl and =VOCl, 1.7 for $–POCl_2$ and $–VOCl_2$, 1,1 for $=TiCl_2$, and 2.1 for $–TiCl_3$. The calculated values (OH_{calc}) satisfactorily fit experimental ones (OH_{exp}): $OH_{exp}/OH_{calc} = 0.98 \pm 0.07$ for PTi silicas and $OH_{exp}/OH_{calc} = 1.12 \pm 0.08$ for PV silicas.

In the electronic diffuse reflection spectrum of PTi silica (Fig. 1), the edge of the charge-transfer absorption band (spectrum *1*) is shifted to the visible region (460 nm) as compared to that (410 nm) of Ti silica (spectrum *2*). Since the surface of the latter contains groups with the titanium coordination number 4, one can conclude that there is an increase of the Ti coordination number in the phosphorus–titanium oxide monolayer. A similar result follows from a comparison of the diffuse reflection spectra of hydrolyzed samples of PTi silica (Fig. 1, spectrum *4*, absorption band edge 385 nm) and Ti silica (Fig. 1, spectrum *5*, 365 nm). According to data in [39], the surface of the hydrolyzed Ti-containing silica gel contains groups with the titanium coordination number, with respect to oxygen, equal to 6 (Fig. 1, spectrum *3*). Calcination at 400°C for 4 h leads results in desorption of water molecules and formation of Ti-containing groups with the titanium coordination number 4 on the surface. Therewith, the edge of the absorption band shifts to short-wave region (365 nm, spectrum *5*). The edge of the absorption band of the hydrolyzed PTi silica (Fig. 1, spectrum *4*) occupies an intermediate position between spectra *3* and *5*. This gives evidence showing that the titanium coordination number is higher than 4 and is caused by formation of a P=O→Ti donor–acceptor bond in a surface group whose structure can be represented, for example, by the scheme

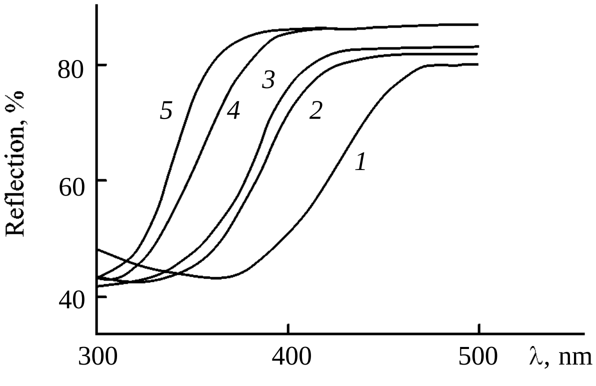
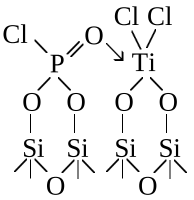


Fig. 1. Diffuse reflection spectra of silicas with modified surface: (*1*) unhydrolyzed phosphorus–titanium-containing silica ([P] 0.61 and [Ti] 0.47 mmol/g_0), (*2*) unhydrolyzed titanium-containing silica ([Ti] 0.52 mmol/g_0), (*3*) hydrolyzed titanium-containing silica, (*4*) hydrolyzed phosphorus–titanium-containing silica, and (*5*) hydrolyzed titanium-containing silica calcined at 400°C for 4 h.



(7)

The X-ray photoelectron spectrum of PTi silica (Fig. 2) is a superposition of bands at 458.2 and 459.7 eV (binding energy E_b of Ti 2*p* electrons). The P=O→Ti bond formation results in electron density transfer to the titanium atom and lowers E_b. Therefore, the band at 458.2 eV can be assigned to titanium

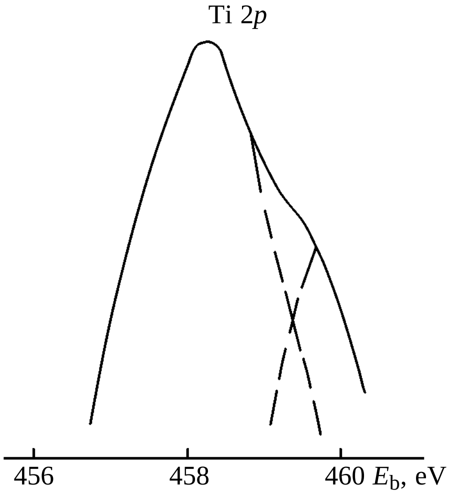


Fig. 2. X-ray photoelectron spectrum of PTi silica. [P] 0.67 and [Ti] 0.47 mmol/g_0.

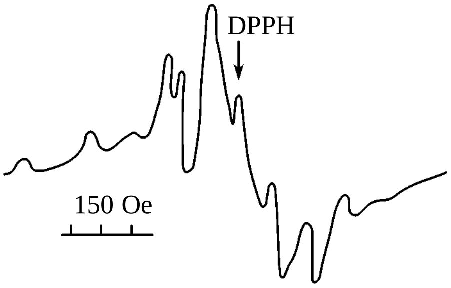


Fig. 3. ESR spectrum of PV silica. [P] 0.69 and [V] 0.42 mmol/g_0.

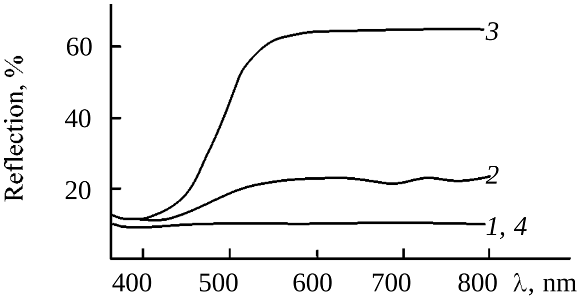


Fig. 4. Diffuse reflection spectra of PV silica. Phosphorus and vanadium concentrations, mmol/g, respectively: (*1*) 0.69 and 0.42; (*2*) 0.12 and 0.78; and (*3*) 0 and (*4*) 1.11. Sample 3 after water sorption.

atoms bound to phosphoryl groups, whose content is 75±15% of the total titanium content of the sample.

In PV silicas, the electron density transfer to the vanadium atom, produced by formation of the P=O→V bond, leads to reduction of V^{5+} to V^{4+}. The ESR spectrum of PV silica (Fig. 3) displays an eight-component structure characteristic of V^{4+} ($g_{\|} = 1.911 \pm 0.002$, $g_{\perp} = 1.992 \pm 0.002$, $A_{\|} = 190 \pm 5$ Oe, $A_{\perp} = 77 \pm 5$ Oe). The spectral parameters give evidence for the presence of V^{4+} in the vanadyl coordination on the surface.

The diffuse reflection spectra of PV silicas are represented in Fig. 4. The spectrum of the V^{5+}-containing silica (Fig. 4, spectrum *3*) contains no absorption band in the visible region. However, the presence of 0.12 mmol/g_0 of phosphoryl groups in the monolayer gives rise to strong absorption in the visible range with ill-defined maxima at 670 and 770 nm (Fig. 4, spectrum *2*). Increase in the phosphorus content results in appearance of continuous structureless absorption in the range 360–800 nm (Fig. 4, spectrum *1*), so that the sample gets black. A similar spectral pattern was earlier observed in the process of water sorption by a vanadium-containing silica [40, 41] (Fig. 4, spectrum *4*), resulting in electron density transfer from the oxygen atom of water molecules to the vanadium atom and reduction of V^{5+} to V^{4+}. The continuous absorption in the visible range is explained by strong cation–cation interactions between closely located vanadium(IV)-containing groups, which causes *d*-electron delocalization [59].

Evidently, a similar process occurs in PV silica; therewith, the role of donor belongs to the phosphoryl oxygen atom.

b. Substitution of Element-containing Groups on Silica by Reactions with Halides

Data on the chemical composition of monolayers and interactions between of functional groups on the surface of synthetic silicas containing vanadium and phosphorus (VP), titanium and phosphorus (TiP), vanadium and titanium (VTi), titanium and vanadium (TiV), chromium and vanadium (CrV), and chromium and titanium (CrTi) were presented in [42–48].

Treatment of Ti silica with $POCl_3$ vapor gives rise to substitution of titanium-containing by phosphoryl chloride groups on the surface. The kinetic curves of the process are depicted in Fig. 5. Chemical analysis of the reaction products shows that, irrespective of the synthesis temperature, the ratio of the amounts of added phosphorus-containing groups to substituted titanium-containing groups (P/ΔTi) is 1.42±0.05, implying occurrence on the following reactions on the surface

$$(\equiv\text{Si–O–})_n\text{TiCl}_{4-n} + \text{POCl}_3 \longrightarrow (\equiv\text{Si–O–})_n\text{POCl}_{3-n} + \text{TiCl}_4, \qquad (8)$$

$$(\equiv\text{Si–O–})_n\text{TiCl}_{4-n} + \text{POCl}_3 \longrightarrow (\equiv\text{Si–O–})_{n-m}\text{TiCl}_{4-n+m} + (\equiv\text{Si–O–})_m\text{POCl}_{3-m}. \qquad (9)$$

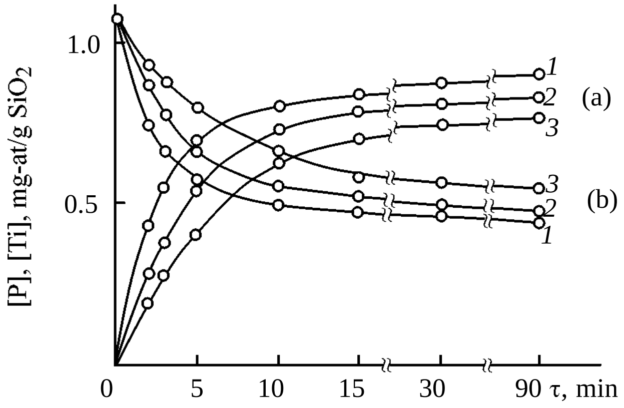


Fig. 5. Time dependence of the element concentration in the solid phase for $POCl_3$ reaction with Ti silica at various temperatures. Element: (a) phosphorus and (b) titanium. Temperature, °C: (*1*) 200, (*2*) 160, and (*3*) 130.

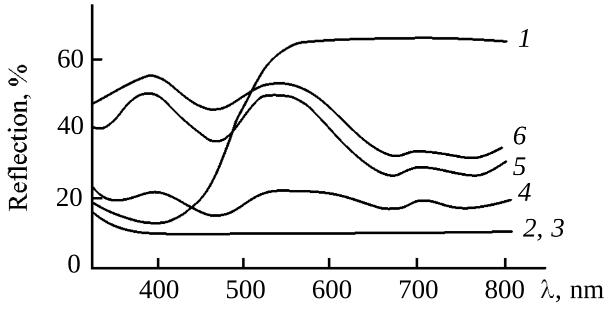


Fig. 6. Diffuse reflection spectra of VP silicas. Vanadium and phosphorus concentrations, mmol/g, respectively: (*1*) V 1.11 and P 0; (*2*) V 0.63 and P 0.59; (*3*) V 0.51 and P 0.73; (*4*) V 0.32 and P 0.93; (*5*) V 0.22 and P 1.04; and (*6*) V 0.12 and P 1.18.

On the basis of reactions (8) and (9) and the initial contents of phosphorus and titanium in the samples, the content of chlorine in the reaction products was calculated by the equation $Cl_{calc} = 1.52 - \Delta Ti + 3\,(P - \Delta Ti)$, where 1.52 is the chlorine content (mmol/g_0) in the initial Ti silica. A good agreement between calculated and experimental values was observed: $Cl_{calc}/Cl_{exp} = 1.00 \pm 0.03$.

The diffuse reflection spectra of TiP silicas are similar to those of PTi silicas of the same chemical composition. This gives evidence for the presence of the complexes shown in scheme (7) in the surface monolayer. The formation of the $P{=}O{\rightarrow}Ti$ donor–acceptor bond decreases the positive charge of the titanium atom and makes titanium-containing groups less susceptible to electrophilic substitution reactions. Therefore, the significant content of titanium in TiP silica (Fig. 5) can be related to interaction between functional groups in the monolayer, which hinders the substitution process. Lowering the synthesis temperature from 200 to 130°CC decelerates the reaction and increase the residual content of titanium from 0.44 to 0.55 mmol/g_0, which is probably associated with increased stability of the complexes shown in scheme (7) [44]. The rate of covering the surface with phosphorus-containing groups is described by the equation

$$d\theta_P/d\tau = K\{1 - (1 + \gamma)\theta_P\}, \tag{10}$$

where θ_P is the coverage degree and $K = 77.3\exp(-15\,000/8.31T)$. The coefficient γ characterizes the decrease in the reactivity of titanium-containing groups, caused by formation of donor–acceptor bonds and is equal to the quantity of titanium-containing groups blocked by one phosphoryl group: $\gamma = (1 - \theta'_P)\theta_P$, where θ'_P is the maximum θ_P at a given temperature. The increase in the stability of the complexes shown in scheme (7) with decreasing synthesis temperature leads to increasing γ.

Treatment of V silica with $POCl_3$ induces the following substitution reactions on the surface [43]:

$$(\equiv Si{-}O{-})_nVOCl_{3-n} + POCl_3 \longrightarrow (\equiv Si{-}O{-})_nPOCl_{3-n} + VOCl_3, \tag{11}$$

$$(\equiv Si{-}O{-})_nVOCl_{3-n} + POCl_3 \rightarrow (\equiv Si{-}O{-})_{n-m}VOCl_{3-n+m} + (\equiv Si{-}O{-})_mPOCl_{3-m}. \tag{12}$$

The $P/\Delta V$ ratio is 1.20 ± 0.03. In the course of the synthesis, the color of VP silicas changes from light yellow ([V] = 1.11, [P] = 0) to black ([V] = 0.63, [P] = 0.59) and bluish-green ([V] = 0.12, [P] = 1.18 mmol/g_0). Parameters of the ESR spectra of VP silicas are identical with those found for PV silicas. The diffuse reflection spectra of VP silicas are given in Fig. 6. In the spectrum of the initial V silica (Fig. 6, spectrum *1*), the absorption band at 380 nm is formed by a charge-transfer transition. Introduction of phosphorus-containing groups into the surface layer gives rise to continuous strucrureless absorption throughout the entire wavelength range (Fig. 6, spectra *2* and *3*). This is caused by $P{=}O{\rightarrow}V$ bond formation, $V^{5+} \rightarrow V^{4+}$ reduction, and by cation–cation interactions between closely located vanadium(IV)-containing groups. The decrease in the vanadium content in the course of synthesis leads to increasing distance between vanadium-containing groups and to appearance of well-resolved absorption bands in the visible

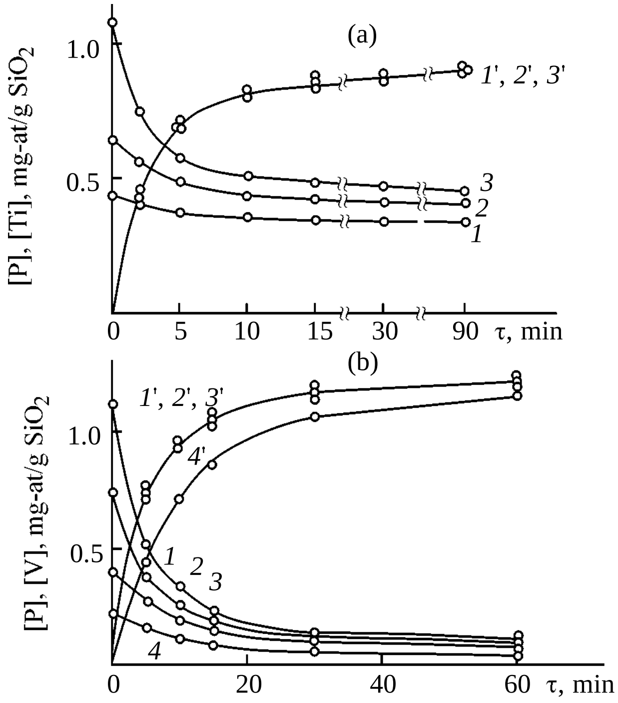


Fig. 7. Time dependence of the element concentration in the solid phase for $POCl_3$ reaction with (a) Ti silica and (b) V silica. (a): (*1, 2,* and *3*) Titanium concentration and (*1', 2',* and *3'*) phosphorus concentration. (b): (*1, 2, 3,* and *4*) Vanadium concentration and (*1', 2', 3',* and *4'*) phosphorus concentration.

range at 460, 670, and 770 nm (Fig. 6, spectra *4*, *5*, and *6*). The band at 460 nm disappears after hydrolysis of the samples, while the positions of the other bands do not change, which allows the former band to be assigned to charge transfer from chlorine to vanadium. The absorption bands at 670 and 770 nm correspond to $^2E_g \rightarrow {}^2A_{1g}$ and $^2Eg_g \rightarrow {}^2B_{2g}$ electron transitions in V^{4+}.

The rate of surface coverage by phosphorus-containing groups is described by Eq. (10) with $\gamma = 0.11$ ($\gamma = 0.74$ for TiP silicas at 200°C) [43]. The lower γ value can be assigned to the lower stability of phosphorus–vanadium oxide complexes with phosphorus–titanium oxide ones. This, together with the higher energy of the Ti–O bond (669 kJ/mol) compared with V–O (532 kJ/mol), is responsible for the decreased residual content of vanadium in VP silica (0.10 mmol/g_0) compared with TiP silica [43, 44].

The concentration of surface hydroxyls increases with decreasing vanadium and titanium contents of the initial V and Ti silicas. Surface hydroxyls can react with $POCl_3$. Figure 7 illustrates the dependence on the reaction time of the phosphorus concentration in the products of $POCl_3$ reaction with Ti and V silicas with various titanium and vanadium contents.

As follows from these data, the decrease of the titanium content of Ti silica to 0.44 and the vanadium content to 0.38 mmol/g_0 has no effect on the rate of surface coverage with phosphorus-containing groups. As products of substitution reactions (8), (9), (11), and (12), $TiCl_4$ and $VOCl_3$ can react with hydroxyls and then again be substituted by phosphorus-containing groups. For example, for vanadium the following reactions can be proposed:

$$(\equiv Si\text{–}O\text{–})_nVOCl_{3-n} + POCl_3 \longrightarrow (\equiv Si\text{–}O\text{–})_nPOCl_{3-n} + VOCl_3, \quad (13)$$

$$m(\equiv Si\text{–}OH) + VOCl_3 \rightarrow (\equiv Si\text{–}O\text{–})_mVOCl_{3-m} + mHCl, \quad (14)$$

$$(\equiv Si\text{–}O\text{–})_mVOCl_{3-m} + POCl_3 \longrightarrow (\equiv Si\text{–}O\text{–})_mPOCl_{3-m} + VOCl_3, \quad (15)$$

etc.

The overall reaction rate is combined of the rates of reactions (13) and (15) ($K = 2.5 \times 10^{-3}$ s^{-1}) and the rate of reaction (14) ($K = 7.8 \times 10^{-3}$ s^{-1}) for VP silicas and of the rates of similar processes for TiP silicas [43, 44]. The rates of reactions (13)–(15) are higher than the rate of $POCl_3$ reaction with OH groups ($K = 3 \times 10^{-4}$ s^{-1}), which explains why the rate of surface coverage with phosphorus-containing groups is independent of the titanium and vanadium contents of the initial silicas.

The decreased reaction rate at [V] = 0.22 mmol/g_0 is caused by decreased amount of $VOCl_3$ formed by reaction (13) and by decreased rate of reaction (14). It is of note that in this case the residual vanadium content is low (0.03 mmol/g_0 or 0.15 wt%), and, therefore, $VOCl_3$ or a vanadium-containing silica gel can be used to promote $POCl_3$ reaction with silica gel [59, 71]. Thus, we deal here with an effect of the third component on the reaction rate, which was also earlier observed in surface reactions [49–51].

The synthesis of a vanadium–titanium oxide monolayer on silica surface was carried out by treatment of V silica with $TiCl_4$ vapor (VTi silicas, Table 6) and, the reverse, by treatment of Ti silica with vanadium oxychloride (TiV silicas, Table 7) [52]. As the experimental results show, the ratios of the amounts of added and substituted groups, Ti/ΔV and V/ΔTi, are close to unity (Tables 6 and 7), and the following substitution reactions occur on the surface

$$(\equiv Si\text{–}O\text{–})_nVOCl_{3-n} + TiCl_4 \longrightarrow (\equiv Si\text{–}O\text{–})_nTiCl_{4-n} + VOCl_3, \quad (16)$$

$$(\equiv Si\text{–}O\text{–})_nTiCl_{4-n} + VOCl_3 \longrightarrow (\equiv Si\text{–}O\text{–})_nVOCl_{3-n} + TiCl_4. \quad (17)$$

Table 6. Chemical composition of VTi silicas

Duration of treatment with $TiCl_4$, min	Content, $mmol/g_0$							Cl_{calc}/Cl_{exp}
	V	Ti	Cl	Ti/V	ΔV	Ti/ΔV	Cl_{calc}	
Initial V silica	1.11	–	0.42	–	–	–	–	–
2	0.61	0.52	0.89	0.84	0.50	1.04	0.94	1.06
3	0.47	0.65	1.05	1.38	0.64	1.02	1.07	1.02
5	0.27	0.84	1.23	3.10	0.84	1.00	1.26	1.02
8	0.11	1.00	1.38	9.08	1.00	1.00	1.42	1.03
10	0.04	1.07	1.50	24.8	1.06	1.01	1.48	0.99
15	0.01	1.10	1.53	110.0	1.10	1.00	1.52	0.99

Table 7. Chemical composition of TiV silicas

Duration of treatment with $VOCl_3$, min	Content, $mmol/g_0$							Cl_{calc}/Cl_{exp}
	Ti	V	Cl	V/Ti	ΔTi	V/ΔTi	Cl_{calc}	
Initial Ti silica	1.08	–	1.52	–	–	–	0.93	–
60	0.85	0.24	1.33	0.28	0.23	1.04	1.28	0.96
120	0.67	0.41	1.12	0.61	0.41	1.00	1.11	0.99
240	0.50	0.59	0.89	1.18	0.58	1.02	0.93	1.04
420	0.39	0.70	0.87	1.80	0.69	1.01	0.82	0.94
540	0.36	0.72	0.85	2.00	0.72	1.00	0.80	0.94

The residual vanadium content of VTi silica is 0.01 $mmol/g_0$, i.e. the substitution is practically complete. This is explained by the absence of interaction between functional groups in the monolayer [52].

The situation is somewhat different in the syntheses of CrV and CrTi silicas [42, 52]. In the latter, by analogy with VTi and TiV silicas, one would expect no surface interactions between functional groups. As shown earlier (see, e.g., [17]), when chromium oxychloride reacts with silica OH groups, $=Cr(O)_2$ groups add to the surface by Si–O–Cr chemical bonds. However, about 40% of hydroxyls of the initial silica prove to be not involved in reaction with CrO_2Cl_2. The surface of such a chromium-containing product acquires pronounced oxidative properties which show up, for example, in reactions with hydrogen. Herewith, the significant residual concentration of OH groups in chromium-containing silica implies their participation, together with $=CrO_2$ groups, in further transformations.

The chemical composition of the initial and synthesized products of treatment of chromium-containing silica with vanadium(V) oxychloride vapor is given in Table 8. As is seen from the table, the vanadium content of the reaction products regularly increases up to 1.2 $mmol/g_0$ and the chromium content correspondingly decreases to a minimum of 0.27 $mmol/g_0$ with increasing time of treatment of chromium-containing silica with $VOCl_3$ vapor. Among gaseous reaction products, CrO_2Cl_2 was found. The concentration of hydroxy groups in the synthesized samples (Table 8) is slightly higher that in the initial samples. The resulting data give evidence showing that the substitution of chromium oxide groups on the surface of chromium-containing silica on its reaction with $VOCl_3$ occurs, for example, by the scheme

$$(\equiv Si–O–)_2CrO_2 + VOCl_3 \longrightarrow (\equiv Si–O–)_2VOCl + CrO_2Cl_2. \qquad (18)$$

If one assumes that only reaction (18) takes place on the surface, the amounts of chemisorbed vanadium (V) and removed chromium (ΔCr) should be equal to each other (as with VTi sample), and the contents of hydroxy groups in hydrolyzed and dried samples should increase by the V value due to the reaction

$$(\equiv Si–O–)_2VOCl + H_2O \longrightarrow (\equiv Si–O–)_2VOOH + HCl. \qquad (19)$$

The experimental data (Table 8) show that the

Table 8. Chemical composition of products of reaction of chromium-containing silica with vanadium oxychloride

Duration of treatment with $VOCl_3$, min	Content, $mmol/g_0$							$[V]/[\Delta Cr]$	Calculated values for OH groups, $mmol/g_0$		$[OH]_{exp}/[OH]_{calc}$
	$[Cr]$	$[\Delta Cr]$	$[V]$	$[V_1]$	$[V_2]$	OH groups in sample					
						$[OH]_{exp}$	$[\Delta OH]_{exp}$		$[OH]_{calc}$	$[OH]_{nr}$	
0	1.03	0	0	0	0	1.50	0	0	1.51	1.51	0.99
5	0.77	0.26	0.27	0.26	0.01	1.65	0.15	1.04	1.75	1.48	0.94
10	0.55	0.48	0.54	0.48	0.06	1.83	0.33	1.12	1.92	1.38	0.95
15	0.41	0.62	0.90	0.62	0.28	1.79	0.29	1.45	1.71	0.94	1.05
28	0.30	0.73	1.22	0.73	0.49	1.86	0.36	1.66	1.74	0.52	1.07
50	0.27	0.76	1.23	0.76	0.47	1.71	0.21	1.62	1.79	0.56	0.96
120	0.27	0.76	1.25	0.76	0.49	1.77	0.27	1.63	1.77	0.52	1.00

[a] $[Cr]$ is the chromium content of the sample; $[\Delta Cr]$ is the amount of chromium removed from the sample by the reaction with $VOCl_3$; $[V]$ is the total amount of chemisorbed vanadium; $[V_1]$ is the amount of vanadium chemisorbed on substitution of $=CrO_2$ groups; $[V_2]$ is the amount of vanadium chemisorbed on the reaction of $VOCl_3$ with ≡Si–OH; $[OH]_{nr}$ is the amount of OH groups not reacted with $VOCl_3$.

V/ΔCr ratio is close to unity only when the vanadium content is lower than 0.5 $mmol/g_0$. At $[V] > 0.5\ mmol/g_0$, the V/ΔCr ratio increases to reach 1.64 ± 0.02 in the final product. Apparently, $VOCl_3$ reacts not only with $(\equiv Si{-}O{-})_2CrO_2$ groups [reaction (18)], but also with surface hydroxyls of chromium-containing silica by the scheme

$$2(\equiv Si{-}OH) + VOCl_3 \longrightarrow (\equiv Si{-}O{-})_2VOCl + 2HCl. \quad (20)$$

As is seen from the above reaction schemes, the content of hydroxy groups in the reaction products should increase with increasing amount of vanadium chemisorbed on substitution of $=CrO_2$ by $=VOCl$ and, further, by $=VOOH$ [schemes (19) and (20)]. The hydroxyl concentration in the samples should by decreased by consecutive reactions (19) and (20). The experimental concentration $[OH]_{exp}$ is $1.76 \pm 0.11\ mmol/g_0$, which indicates simultaneous reactions of $VOCl_3$ with the chromium-containing silica by schemes (18) and (20). The slightly increased hydroxyl concentrations in the synthesized products suggest that reaction (18) is faster than reaction (20).

The amount of hydrogen chloride evolved, according to reaction (20), per unit time from one gram of an initial sample is $C_{HCl} = 0.49 \cdot 2/28 = 0.035\ mmol\ g_0^{-1}\ min^{-1}$. The analogous value for the synthesis of chromium-containing silica gel is $C_{HCl} = 1.03 \cdot 2/60 = 0.034\ mmol\ g_0^{-1}\ min^{-1}$. Hydrogen chloride formed in the latter synthesis does not cleave the Si–O–Cr bond, and the resulting silica gel contains 1.03 $mmol/g_0$ of chromium. Presumably, hydrogen chloride formed by reaction (20), too, exerts no effect on the stability of $(\equiv Si{-}O{-})_2CrO_2$ groups. It is evident, however, that HCl formed by reaction (20) is able to partially reduce Cr^{6+} to Cr^{3+} on the surface to form groups resistant to hydrogen chloride. Apparently, the above redox process causes the incomplete substitution of chromium-containing groups by vanadium-containing in the reactions of the initial samples with vanadium oxychloride [schemes (18) and (20)].

The addition of vanadium-containing groups with formation of two Si–O–V bonds on substitution of $=CrO_2$ [scheme (18); Figs. 8a, 8b, 8c, and 8d] is apparently caused by a certain structural similarity of the tetrahedral surface groups $=CrO_2$ (Fig. 8c) and $=VOCl$ (Fig. 8d), as well as by the geometrical similarity of the CrO_2Cl_2 (Fig. 8b) and $VOCl_3$ molecules (Fig. 8a) having the shape of slightly distorted tetrahedra with close values of bond lengths and angles [42, 52]. The fact that vanadium oxychloride reacts with residual hydroxyls of chromium-containing silica gel by its two chlorine aroms agrees with data on the effect of hydroxylation degree of silica surface in $VOCl_3$ reaction with silica on the composition of the resulting vanadium oxychloride groups.

Thus, the above experimental results and their analysis allow the following conclusions. The reaction of chromium-containing silica gel with vanadium oxychloride involves consecutive-concurrent substitutions of $=CrO_2$ and H^+ in $(\equiv Si{-}O{-})_2CrO_2$ and ≡Si–OH groups by $=VOCl$ to form $(\equiv Si{-}O{-})_2VOCl$. Herewith, $=CrO_2$ groups are removed from the surface mostly via reactions (18), whereas $=VOCl$ groups are formed on the surface both via reaction (18) and via reaction (20). The latter is confirmed by increased V/ΔCr

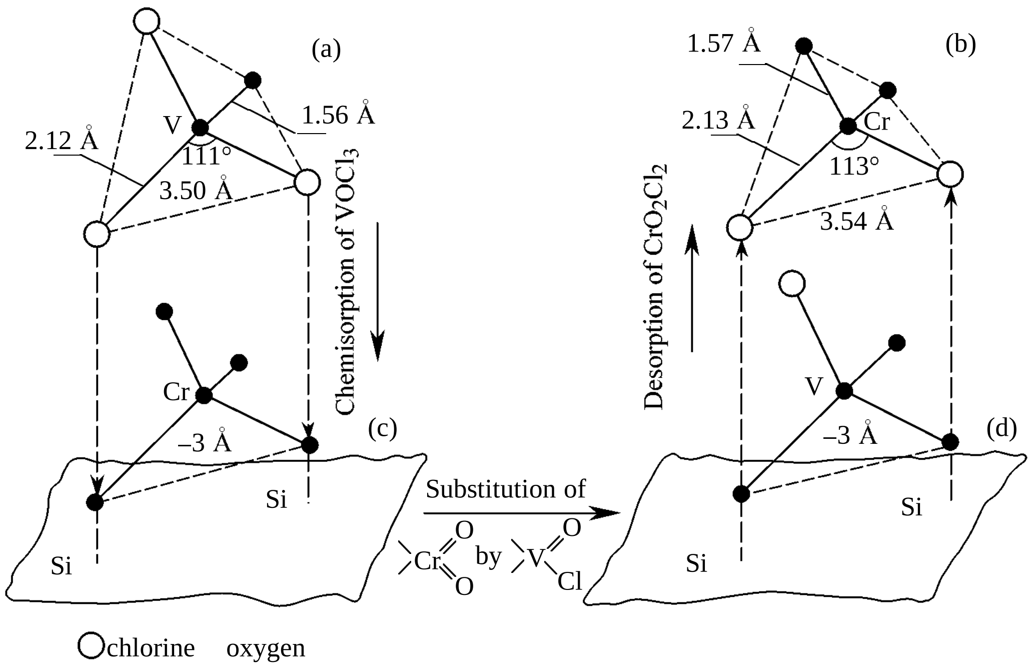


Fig. 8. Geometrical dimensions of the tetrahedral molecules of (a) $VOCl_3$ and (b) CrO_2Cl_2 and of the surface groups (c) =CrO2 and (d) =VOCl.

ratio, by almost equal contents of OH groups (1.76 ± 0.11 mmol/g_0) in hydrolyzed and dried samples, and by decreased amount of OH groups not reacted with $VOCl_3$ ($[OH]_{nr} = 0.53 \pm 0.02$ mmol/g_0) (Table 8).

On the basis of the proposed schemes of $VOCl_3$ reaction with the surface of chromium-containing silica surface, contents of OH groups in hydrolyzed and dried samples, $[OH]_{calc}$, were estimated and compared with experimental values, $[OH]_{exp}$. The $[OH]_{exp}/[OH]_{calc}$ ratio is close to unity for all reaction stages, which confirms the proposed schemes (18)–(20).

Similar results were obtained for the synthesis of CrTi-containing silica [52]. The amount of chromium in the final sample of the CrTi silica obtained by treatment of Cr silica with $TiCl_4$, is 0.38 mmol/g_0 (~37% of the initial amount) at the surface titanium concentration 1.26 mmol/g_0. However, chromium-containing groups in the CrTi sample contain a significant amount (0.33 mmol/g_0 from the total amount (0.38 mmol/g_0) of trivalent chromium which is evident to be stable to $TiCl_4$. The increase of the Cr^{3+} content in the course of the synthesis of the CrTi-product, as compared with its concentration in the initial chromium-containing silica ($\leq$ 0.05 mmol/g_0), is evidently caused by reduction of Cr^{6+} on the surface, with formation of $(\equiv Si–O–)_2CrOH$ groups, by gaseous hydrogen chloride that is liberated in the course of reaction of $TiCl_4$ with OH groups of chromium-containing silica gel (as in the synthesis of CrV silica).

c. Selective Chemisorption from a Mixture of Halide Vapors at Forming a Two-component Monolayer on Silica

The experiments were carried out with $TiCl_4$ and $VOCl_3$ at molar ratios in the gas phase of 0.6 (Fig. 9a) and 1.5 (Fig. 9b) and a total concentration of 0.4 mol/m^3. According to [53], $TiCl_4$ and $VOCl_3$, in contrast with $POCl_3$ and $TiCl_4$, as well as $POCl_3$ and $VOCl_3$, do not form chemical compounds with each other. Analysis of experimental data revealed the following consecutive–concurrent reactions on silica gel surface [59]:

$$n(\equiv Si–OH) + VOCl_3 \xrightarrow{K_1} (\equiv Si–O–)_nVOCl_{3-n} + nHCl, \quad (21)$$

$$m(\equiv Si–OH) + TiCl_4 \xrightarrow{K_2} (\equiv Si–O–)_mTiCl_{4-m} + mHCl, \quad (22)$$

$$(\equiv Si–O–)_nVOCl_{3-n} + TiCl_4 \xrightarrow{K_3} (\equiv Si–O–)_nTiCl_{4-n} + VOCl_3. \quad (23)$$

The dependence of the content of vanadium and titanium in the products on the rection time is described by the equations

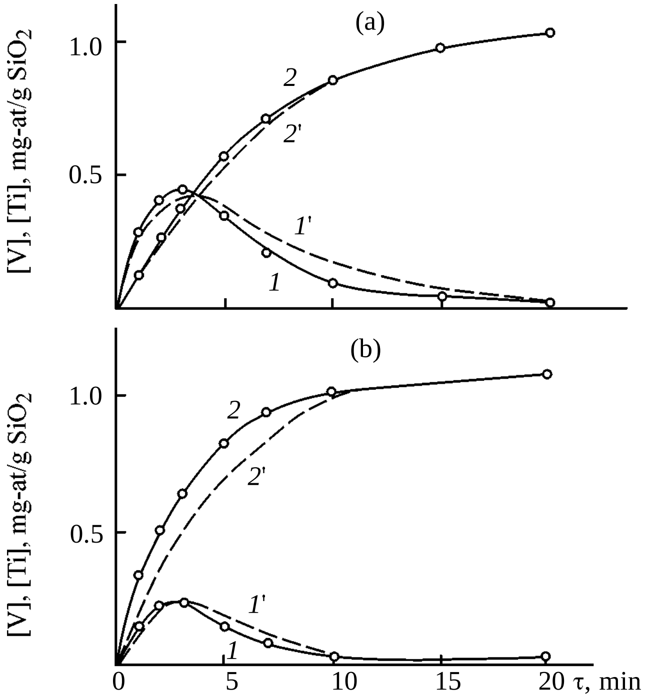


Fig. 9. Kinetic curves for silica gel reaction with a mixture of $VOCl_3$ and $TiCl_4$ vapors. $TiCl_4/VOCl_3$: (a) 0.6 and (b) 1.5. (*1*) Vanadium concentration, (*2*) titanium concentrations, and (*1'*, *2'*) calculated curves.

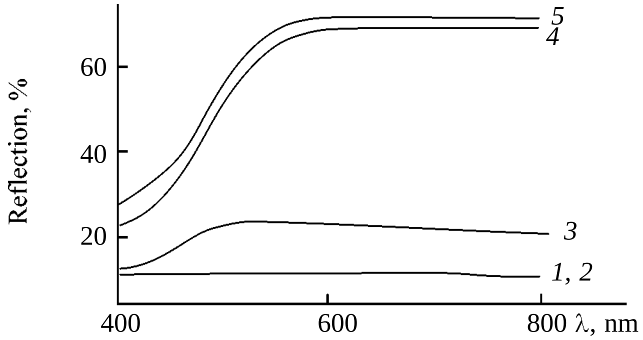


Fig. 10. Diffuse reflection spectra of PTiV silicas. Phosphorus, titanium, and vanadium concentrations, mg-at/g, respectively: (*1*) 0.26, 0, and 0.26; (*2*) 0.28, 0.12, and 0.28; (*3*) 0.30, 0.20, and 0.20; (*4*) 0.26, 0.27, and 0.30; and (*5*) 0.28, 0.28, and 0.15. The spectra numbering corresponds to the sample numbering in Table 9.

$$\theta_V = [k'_1/(k'_1 + k'_2 - k'_3)]\{\exp(-k'_3\tau) - \exp[-(k'_1 + k'_2)]\}, \quad (24)$$

$$\theta_{Ti} = (1 - k'_1/(k'_1 + k'_2 - k'_3)\{\exp(-k'_3\tau) - \exp[-(k'_1 + k'_2)]\}) - \exp[-(k'_1 + k'_2)\tau], \quad (25)$$

where $k'_1 = k_1[VOCl_3]/([VOCl_3] + [TiCl_4])$, $k'_2 = k_2[TiCl_4]/([VOCl_3] + [TiCl_4])$, and $k'_3 = k_3[TiCl_4]/([VOCl_3] + [TiCl_4])$. The kinetic curves of separately taken reactions (21)–(23) yield the values $k_1 = 7.8 \times 10^{-3}$ s^{-1}, $k_2 = 4.7 \times 10^{-3}$ s^{-1}, and $k_3 = 7.5 \times 10^{-3}$ s^{-1}. By substituting these values and the ratios $[VOCl_3]/([TiCl_4] + [VOCl_3]) = 0.63$ and $[TiCl_4]/([TiCl_4] + [VOCl_3]) = 0.38$ (Fig. 9a) and, correspondingly, 0.4 and 0.6 (Fig. 9b) in Eqs. (24) and (25), we obtain estimated curves (Fig. 9). Least-squares treatment gave the following rms deviations of the estimated curves from experimental: S_{θ_V} = 9% and $S_{\theta_{Ti}}$ = 5% (Fig. 9a) and S_{θ_V} = 5% and $S_{\theta_{Ti}}$ = 12% (Fig. 9b).

Thus, Eqs. (22) and (25) satisfactorily describe the reaction of a mixture of $VOCl_3$ and $TiCl_4$ with silica gel. It follows from Fig. 9 that at sufficiently long reaction times $TiCl_4$ is almost selectively chemisorbed by silica gel. This implies the possible utility of such processes for separation and purification of chlorides [54].

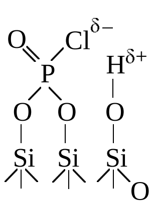
INTERACTION OF FUNCTIONAL GROUPS IN THE THREE-COMPONENT PHOSPHORUS–TITANIUM–VANADIUM OXIDE MONOLAYER ON SILICA GEL

Evdokimov *et al.* [55] synthesized PTiV silicas by treatment of PTi silica with $VOCl_3$ vapor (Table 9) and studied interfunctional interactions in the three-component monolayer.

Based on the structure of the phosphorus–titanium oxide complex in PTi silicas, represented by scheme (7), one can suppose that, under at P/Ti > 1, part of phosphorus oxide groups is not bound with the titanium atom and can form, on treatment with $VOCl_3$ of PTi silicas possessing reactive OH groups, a donor–acceptor bond with the vanadium atom. Herewith, a three-component element oxide monolayer is realized on the silica surface. If, however, P/Ti ≤ 1, introduction of vanadium oxide groups in the monolayer should not lead to bounding vanadium with phosphoryl groups.

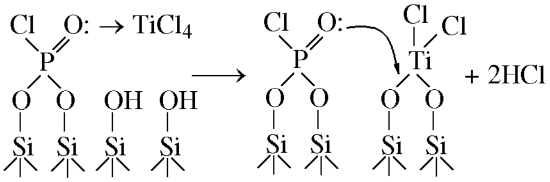
Similar reasoning can be applied to PV silicas treated with $TiCl_4$. In this case, however, the interaction will be complicated by substitution reaction of vanadium-containing groups with titanium tetrachloride. The diffuse reflection spectra of the samples are depicted in Fig. 10. As follows from data in Table 9, the samples change in color from black to yellow as the P/Ti ratio is varied (at the vanadium content 0.2 to 0.3 $mmol/g_0$). The appearance of a black or dark brown color (strong absorption in the visible range, Fig. 10, spectra *1*–*3*) is evidently caused by vanadium reduction with phosphoryl groups not bound with titanium. At P/Ti ≤ 1 (Table 9, samples 4 and 5), practically all phosphoryl groups are involved in the $P{=}O{\rightarrow}Ti$ donor-acceptor bond and do not react with vanadium-containing groups. In this case, the diffuse reflection spectra (Fig. 10, spectra *4* and *5*) represent a superposition of charge-transfer bands in phosphorus–titanium oxide complexes and in vanadium oxide groups (the band edges lie at 460 and 540 mm, respectively).

It should be noted that the concentration of OH groups in the P silica with a phosphorus content of 0.26 mmol/g_0 is 2.88 mmol/g_0. Therefore, in the case of a statistically uniform distribution of 0.26 mmol/g_0 of titanium-containing groups added, part of phosphorus oxide groups will be located at sufficiently large distances from titanium oxide ones [59]. However, as follows from the above data, practically all phosphoryl groups are bound with titanium atoms by a donor–acceptor bond. Therefore, titanium-containing groups are added by hydroxyls located near phosphorus-containing groups. Such a mechanism of addition can be caused by the inductive effect of ≡PO and =POCl groups according to scheme (26):


(26)

This effect enhances the reactivity of hydroxyls in electrophilic substitution reactions.

The inductive effect can also be strengthened by that the donor–acceptor bond is formed first and then the hydroxyl proton is substituted by a titanium-containing group:


(27)

The initial formation of the donor–acceptor bond [scheme (27)] shifts the electron density from the phosphoryl oxygen to titanium, and, as a consequence, to a still stronger protonation of the neighboring hydroxyl group according to scheme (26).

Thus, the formation of a donor-acceptor bond in the synthesis of PTi silicas plays an essential role in building a two-component monolayer, and the titanium-containing groups synthesized are placed near the phosphoryl chloride groups existing on the surface. Vanadium-containing groups are added with no formation of the P=O→V donor-acceptor bond in the synthesis of a three-component element oxide monolayer (PTiV silicas) at P/Ti ≤ 1 [55].

Table 9. Chemical composition and color of PTiV silicas

No.	Element content, mmol/g_0				Color
	P	Ti	P/Ti	V	
1	0.26	–	–	0.26	Black
2	0.28	0.12	2.3	0.28	″
3	0.30	0.20	1.5	0.20	Dark brown
4	0.26	0.26	1.0	0.30	Light yellow
5	0.28	0.38	0.7	0.15	″

It is of note that the above schemes of chemical reactions resulting in formation of multicomponent oxide mono- and multilayers on silica surface, are idealized to a certain extent. However, the schemes are suggested on the basis of thorough chemical-analytical investigations by modern physicochemical methods both in our work and in the literature and give an outline of the main direction of the chemical interaction under study and the functional composition of surface structures.

Together with published data, the experimental data reviewed show that chemical reactions in molecular layering processes are presently explored sufficienly to be used as the basis for creating a new synthetic technology. It view of the reasoning of Tret'yakov and Lepis [7], there are good grounds to believe that chemical engineers are sufficiently armed by "fundamental chemical principles determining basic chemical possibilities of acting on materials" with the aid of the molecular layering method. Indeed, some data are now available on the effect of multicomponent low-dimensional systems on the functional properties of solid-phase materials. Thus, phosphorus–vanadium–(chromium) oxide synergistic structures that improve thermal-oxidative characteristics of epoxyphenol and phenol–formaldehyde polymeric compositions have been reported, as well as two- and three-component titanium–phosphorus–chromium oxide multifunctional nanolayers with various mutual location of the components on the surface of microspherical glass fillers for spheroplasts, iron–zinc oxide pigment nanocoatings on the surface of fine silicon oxide particles, titanium–silicon oxide nanoadditives on the surface of preceramic materials accelerating solid-phase chemical reactions, etc. [23, 31, 32].

EXPERIMENTAL

Oxychlorides and chlorides of ultrapure and chemically pure grades [56] were used in synthetic experiments. Purified silica gel (specific surface area 250 m^2/g, average pore diameter 14 nm) was used as carrier.

Two-component samples were synthesized in a flow device in a dry carrier gas under the conditions described in [12, 29, 44]. Final reaction products were analyzed for initial and chemisorbed elements by the procedures described in [57–61].

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