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Quantum-Chemical Analysis and Experimental Study of the Process of the Silica Surface Interaction with the CrO_2Cl_2 and $VOCl_3$ Vapor Mixture

A. N. Gukova, S. D. Dubrovenskii, and A. A. Malygin

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: dubroven@lti-gti.ru

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Abstract—We accomplished a synthesis of the two-component vanadium–chromium containing monolayer on the silica surface by treating the latter with a mixture of CrO_2Cl_2 and $VOCl_3$ vapors. Analysis of the chemical reactions on the substrate surface is carried out using quantum-chemical modeling. The calculated $VOCl_3$ reactivity is higher than that of CrO_2Cl_2, which requires the use of an excess of the chromium oxychloride in the reaction mixture to provide a control over the coating composition in a wide range of concentrations. The quantitative forecast of the reaction product composition indicates a significant role of the synthesis temperature and structural strain at the formation of the monolayer. We carried out an experimental synthesis of the two-component coating by the method of molecular layering (ML) under the conditions derived from quantum-chemical predictions, at a concentration ratio of chromium and vanadium in the range from 0.5 to 2.6, and showed the ability of control over the product composition. Based on a comparison of experimental and calculated data the structural strains and the quantitative ratio of the surface centers of different local structure were estimated. The results obtained using infrared Fourier spectroscopy confirm the agreement between the experimental data and the quantum-chemical predictions.

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Vanadium oxide and chromium oxide coatings applied by different methods to the surface of solid matrices are widely used as catalysts for mild oxidation and dehydrogenation [1, 2]. It was noted in particular [3–5] that their catalytic activity and selectivity increases sharply at the monolayer coverage of the carrier surface with isolated element oxide centers. Such structures can be formed by molecular layering (ML) [6], for example, in the gas-phase flow systems with the use as reagents of $VOCl_3$ [7] and CrO_2Cl_2 vapors [8], followed by replacement of OH groups for chlorine atoms by the treatment with water vapor [Eqs. (1), (2)].

$$n(\equiv Si–OH) + VOCl_3 \rightleftarrows (\equiv Si–O)_nVOCl_{3-n} + n\,HCl, \quad n = 1, 2, 3, \qquad (1)$$

$$n(\equiv SiOH) + CrO_2Cl_2 \rightleftarrows (\equiv SiO)_nCrO_2Cl_{2-n} + n\,HCl, \quad n = 1, 2. \qquad (2)$$

The value of n, meaning functionality, characterizes the number of bonds Si–O–E in the formed centers and depends on the genesis, composition, and structure of the matrix surface, as well as on the conditions of the synthesis [9, 10].

On the other hand, there is a growing interest in the development of multicomponent catalytic systems and coatings with enhanced activity and selectivity [1, 11–13]. This also concerns the mixed vanadium–chromium oxide systems [1, 12]. In this connection it is interesting to investigate a possibility of the synthesis of monolayer chromium–vanadium-containing nano-coatings on the silica surface.

The preparation of such coating meets significant methodological difficulties. First of all, this is connected with the necessity to carry out a complex of chemical transformations on the carrier surface, involving multiple molecular reagents and controlled by various external factors: the duration of the carrier processing, temperature, and the ratio of reactants in the gas phase [6]. In comparison with the one-component coatings the complexity of identifying composition and structure of the obtained coatings also significantly increases. To resolve all these challenges,

it seems appropriate to involve the quantum-chemical approaches that can be effective for predicting the structure of the synthesized surface centers [14].

Such studies have been already carried out for the mixed titanium–vanadium–phosphorus oxide monolayer on the surface of silica [6, 15–18]. Thus, these two-component systems can be obtained by sequential processing of the carrier with different reagents. For example, vanadium oxychloride groups obtained by processing silica in accordance with the scheme (1) can be replaced by the titanium–oxychloride under the action of the vapor of the more reactive $TiCl_4$:

$$(\equiv SiO)_nVOCl_{3-n} + TiCl_4 \rightleftarrows (\equiv SiO)_nTiCl_{4-n} + VOCl_3. \quad (3)$$

It has been shown in [6] that the reaction (3) is reversible. Performing the process under nonequilibrium conditions, for example, at a constant feed to the reaction zone of $VOCl_3$ vapor and removal of $TiCl_4$, can lead to the complete replacement of one modifier by another. As a result, one of the decisive factors for the control over composition of such multicomponent systems is the duration of processing with the second and subsequent reagents. An additional problem at the sequential processing is the possibility of appearance of the concentration gradients in the coating composition. For example, at the carrying out the synthesis in the fixed layers of a dispersed material a gradient can appear across the layer height due to the difference in the duration of contact of the reagent with grains. For the same reason in porous media in the presence of intra-diffusion inhibition, the composition may vary across the grain depth.

The alternative is to perform the interaction of the substrate surface points with a mixture of reactant vapors, which can be represented as a set of parallel and consecutive reactions, for example, by the schemes (1), (2) and (4).

$$(\equiv SiO)_nCrO_2Cl_{2-n} + VOCl_3 \rightleftarrows (\equiv SiO)_nVOCl_{3-n} + CrO_2Cl_2. \quad (4)$$

After the time required for processing with the reagents, the system reaches a steady state [6]. The composition of the products obtained is determined by the relative reactivity of the precursor molecules and the ratio of their concentrations in the gas phase. The reactivity, in turn, depends on temperature.

Thus, it is possible to assume that for a homogeneous binary V–Cr coating a treatment of silica with a mixture of $VOCl_3$ and CrO_2Cl_2 vapors is preferred. After the exhaustion of surface ≡Si–OH groups in the reactions (1) and (2) it is presumable by analogy with the system Ti–V [6] that the processes of reversible substitution of chromium-containing groups by the vanadium ones and vice versa would occur [Eq. (4)].

Then at a given temperature the product composition will be determined by the concentrations of the molecular reagents, and the forecast of the coating composition can be obtained using the apparatus of equilibrium thermodynamics. The interconnection of the components ratio in the coating and in the gas phase is determined by the equilibrium constants K:

$$K_n = \frac{[CrO_2Cl_2]_g[(\equiv SiO)_nVOCl_{3-n}]_{sol}}{[VOCl_3]_g[(\equiv SiO)_nCrO_2Cl_{2-n}]_{sol}}. \quad (5)$$

The value of the equilibrium constant of a separate reaction can be estimated from the linear approximation of the experimental relationship between the ratios of molar concentrations of the elements modifiers in the solid (β) and in the gas phase (α):

$$\beta = [(\equiv SiO)_nCrO_2Cl_{2-n}]_{sol}[(\equiv SiO)_nVOCl_{3-n}]_{sol},$$
$$\alpha = [CrO_2Cl_2]_g/[VOCl_3]_g,\ \alpha = K_n\beta. \quad (6)$$

However, for the considered system the factor of functionality must also be taken into account. For example, at the processing the silica surface with the vanadium oxychloride vapor centers can form with the number of SiO–V bonds from 1 to 3 [7, 10] (Fig. 1a), while at the interaction with chromium oxychloride mono- and bifunctional groups can form [8] (Fig. 1b). It is obvious that the values of equilibrium constants K_n of reactions (4) for the structures with different functionality (different n) will be the same or even close. Moreover, on the surface of SiO_2 may also occur the processes of change in functionality, for example, according to Eqs. (7) and (8).

$$3\,(\equiv SiO)_2CrO_2 + 2\,VOCl_3 \rightleftarrows 2\,(\equiv SiO)_3VO + 3\,CrO_2Cl_2, \quad (7)$$
$$2\equiv SiOCrO_2Cl + VOCl_3 \rightleftarrows (\equiv SiO)_2VOCl + 2\,CrO_2Cl_2. \quad (8)$$

Thus, in the process of the synthesis of vanadium–chromium coatings many competing routes of chemical transformations can appear that strongly impede obtaining empirical estimates of the thermodynamic characteristics.

On the other hand, such estimates can be obtained using quantum-chemical models based on the previously developed technique [14].

With these models we carried out calculations of the equilibrium concentration fields in the approxima-

tion of the closed isobaric–isothermal system at different temperatures under atmospheric pressure with accounting for the phase equilibria. The initial amount of reactants in the reaction volume was 1 mol of silanol groups fixed on the SiO_2 surface, 2 mol of $VOCl_3$ vapor, and 1 to 20 mol of chromium oxychloride vapor, which corresponds to the interval of varying α from 0.5 to 10. Calculations of equilibrium composition of the products of interaction were performed for the temperature range 273–673 K, where the degree of dehydroxylation of SiO_2 surface is small and the silanol groups mostly remain vicinal [19].

The forecast using the minimal model without taking into account the structural strains (Figs. 2a, 2b) showed that the reactivity of $VOCl_3$ with respect to the active centers on the silica surface is much higher than that of CrO_2Cl_2. This result is consistent with the data of [20]. In accordance with the results of thermodynamic calculations, the silica surface should be filled almost exclusively with the trifunctional vanadium–oxide centers V_{III} (Fig. 3a), because their formation, without taking into account the structural strain, is energetically most advantageous. The proportion of groups V_{II} and V_I in the coating is significantly lower (10^{-2} and 10^{-3}, respectively). The total percentage of the chromium-containing centers does not exceed 10^{-4}. This result is consistent with the nessecity to use chromium oxychloride in a significant excess ($\alpha \approx 10^4$)

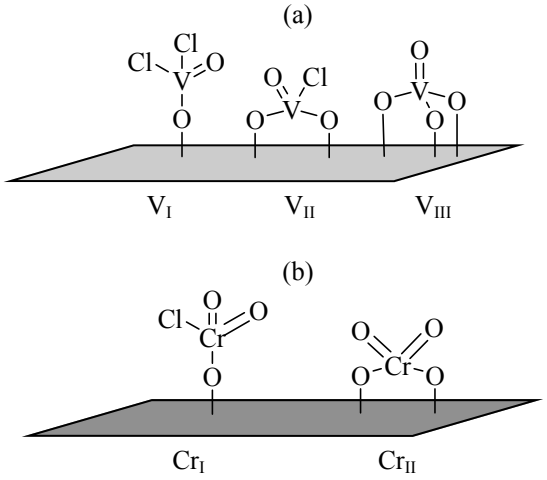

Fig. 1. (a) Vanadium- and (b) chromium- containing groups on the silica surface: (X_I) monofunctional, (X_{II}) bifunctional, (X_{III}) trifunctional .

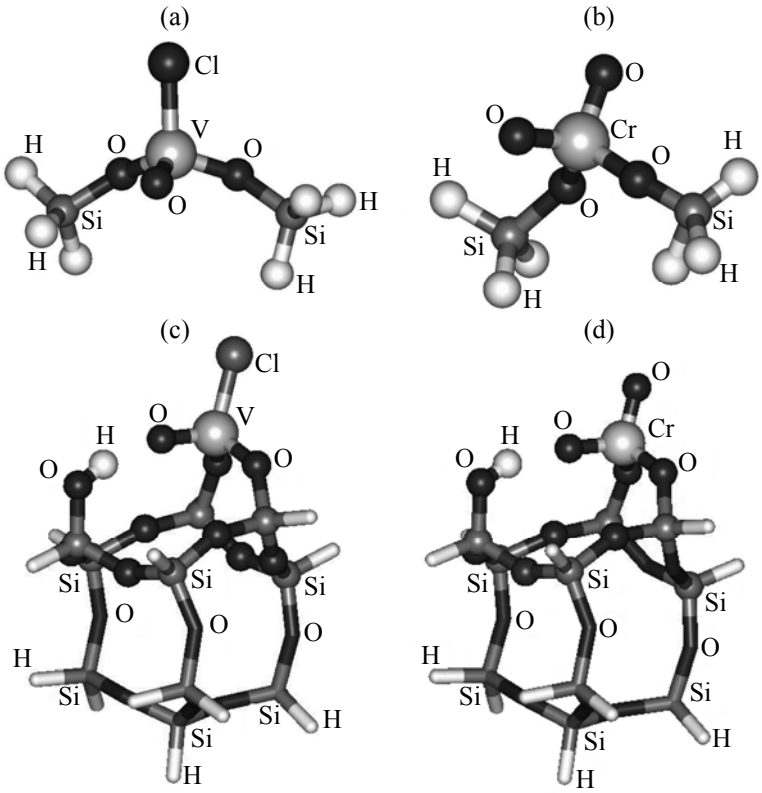

Fig. 2. Optimized cluster models of (a, c) vanadium and (b, d) chromium containing groups on the example of bifunctional centers: (a, b) models of the minimum size and (c, d) of closed clusters on the basis of section (111) of β-cristobalite.

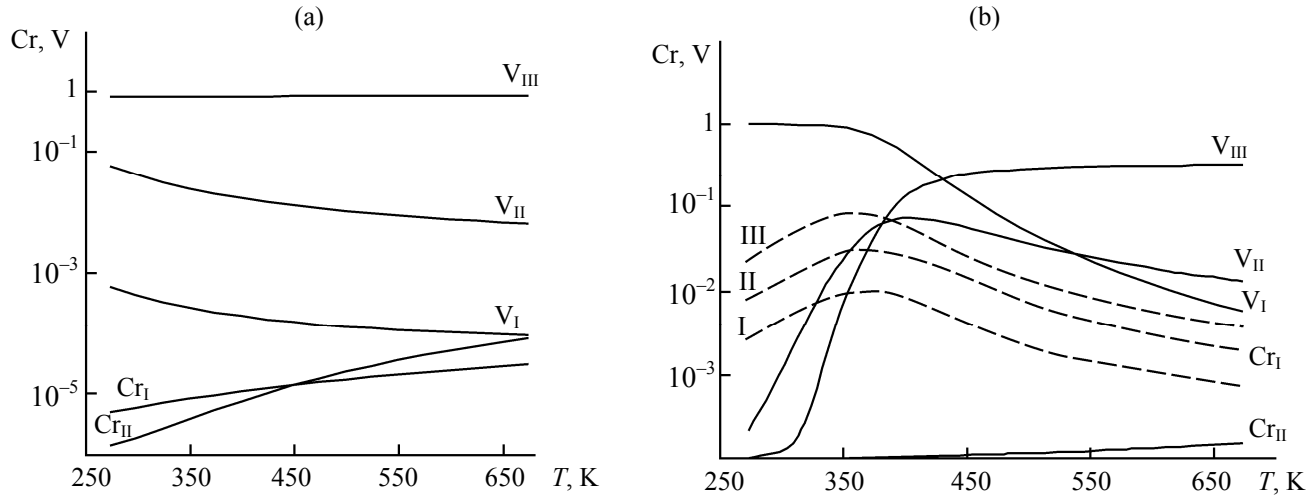

Fig. 3. Calculated dependences of the content of the element-oxide groups of different functionality vs. the synthesis temperature: (a) without steric strain, (b) taking into account the steric strain 95, 50, and 60 kJ mol^{-1} for the centers of V_{III}, V_{II}, and Cr_{II}, respectively. Here and below the following notations are used: the molar ratios of the reactants in gas phase: I, $\alpha = 1$; II, $\alpha = 3$; III, $\alpha = 6.5$; Cr, V are numbers of chromium and vanadium containing groups, respectively, per one active center on the silica surface.

in the gas phase to produce coatings with the equal contents of chromium and vanadium.

At the same time, for multifunctional centers significant structural strains in the surface layer of silica can be expected, whose values depend on the local structure of its surface. One of the most common is a structural model based on the crystallographic section (111) of β-cristobalite [21]. The calculations for the cluster models of this type, containing 10 silicon atoms (Fig. 2c), show a decrease in energy gain at the formation of groups V_{III}, V_{II}, and Cr_{II} by 95, 50, and 60 kJ mol^{-1}, respectively. These values can be regarded as estimated values of steric strains arising at the formation of closed element–siloxane cyclic fragments. The thermodynamic calculations with taking them into account showed that at the temperatures up to 350 K the formation of monofunctional V_I centers should be expected, while multifunctional V_{III} and V_{II} centers are formed in appreciable amounts above 450 K (Fig. 3b). Thus, the thermodynamic probability of formation of multifunctional groups is reduced by the steric strain. This reduction is especially significant for the three-functional vanadium-containing groups, which leads to an increase in the proportion of chromium-containing centers to 0.01–0.1. The steric strain also leads to an extreme temperature dependence of the chromium content with a peak at 350 K. Therewith, the formation of monofunctional groups Cr_I is energetically more favorable for they do not create strains in the surface layer. Furthermore, in contrast to the results obtained in the absence of strains (Fig. 3a), a pronounced dependence of the chromium content on the value of α is predicted which confirms the possibility of control over the composition of the coating by varying α, the ratio of gas-phase reagents. As a result, the estimated excess of CrO_2Cl_2 required to achieve the values of $\beta \sim 1$ is reduced by three orders of magnitude and corresponds to the value $\alpha \approx 15$–20.

Unfortunately, to date the information about the structure of the real surface of the porous silica is quite insufficient for precise modeling taking into account steric strain at the formation of multifunctional groups. Nevertheless, the calculated results helped to determine the range of temperatures and concentrations at which it is possible to control the composition of two-component coating.

The initial matrix for obtaining samples of chromium–vanadium containing coating was silica gel brand ShSKG. The source of gaseous reactants was a mixture of liquid oxychlorides. Molar ratio of reagents in the gas phase α was controlled by mixing liquid oxychlorides in different proportions. As shown by test experiments, the stationary composition of the coating is achieved in 2 h or less at the contact of the material with a mixture of reactants vapor.

We synthesized a series of samples by varying the ratio α from 2.5 to 6.5, which allowed us to obtain coatings with the molar ratio of modifier β from 0.5 to

Table 1. Composition of the reaction mixture and the samples obtained[a]

Concentration in the gas phase, mol l^{-1}		Reagents ratio, $\alpha = [Cr]/[V]$	Concentration in the solid phase, mmol per 1 g of SiO_2		Ratio of components in the solid phase, $\beta = [Cr]/[V]$
[Cr]	[V]		[Cr]	[V]	
0.32	0.13	2.5	0.41	0.79	0.5
0.075	0.025	3.0	0.51	0.85	0.6
0.07	0.02	3.5	0.52	0.80	0.7
0.38	0.09	4.2	0.59	0.61	1.0
0.34	0.08	4.3	0.71	0.57	1.3
0.43	0.08	5.4	0.72	0.40	1.8
0.48	0.07	6.9	0.86	0.32	2.7

[a] Measuring error 7%.

2.6 (Table 1). It follows from these data that the proportion of chromium in the products of the synthesis β varies in parallel with the ratio of gas-phase reagents concentrations, α.

It should be noted that the ratio of the modifiers of the coatings $\beta \sim 1$ is reached even at lower CrO_2Cl_2 excess in the gas phase than predicted by the models on the basis of β-cristobalite section (111). Apparently, the calculated estimates of steric strain for such models do not fully correspond to the real surface of silica gel due to the differences in its local structure and the structure of the crystal surface. In this connection, it is of interest to estimate the magnitude of steric strain providing the best agreement between the calculated and experimental data.

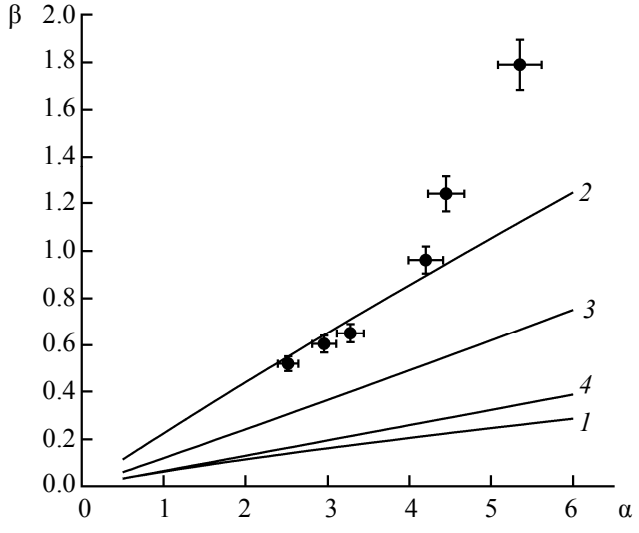

Fig. 4. Experimental (dots) and calculated (lines) dependences of α on β at different temperatures, K: (*1*) 373, (*2*) 473, (*3*) 573, and (*4*) 673.

For this purpose we varied steric strain values used in the thermodynamic prediction of the coating composition to achieve the lowest standard deviation of the calculated and experimental dependences β(α). The minimum deviation was achieved at the values of the strain energy 95, 70, and 23 kJ mol^{-1} for the centers of V_{III}, V_{II}, and Cr_{II}, respectively (Fig. 4). Increase in the deviation for the values of $\beta > 1$ may be due to the occurrence of alternative chemical transformations, for example, redox, in addition to schemes (1), (2), and (4). The forecast of the composition of vanadium–chromium-bearing monolayer with accounting for functionality under these conditions (Fig. 5) showed that up to 350 K dominate monofunctional vanadium groups, in the range of 400 to 490 K, mono- and three-dentate vanadium-containing groups are formed with approximately equal probability, and in the region above 490 K dominate trifunctional centers (Fig. 4a). According to calculations, the chromium-containing groups are formed in appreciable quantities at a temperature above 350 K, and they are bifunctional centers mainly (Fig. 5b). For the temperature above 450 K is predicted a decrease in the chromium content in the reaction product. Note that the estimated chromium fraction in the coating reaches a maximum at a temperature of 450 K, which is consistent with the temperature of the synthesis.

Quantum-chemical calculation of vibration states of the grafted surface groups taking into account anharmonic effects provides also a possibility of semi-quantitative prediction of IR spectra [14]. The results obtained (Table 2) can be used to identify the local structure of the surface centers by IR spectroscopy. According to calculation [14] and experimental data [22], the absorption band of the double bonds E=O

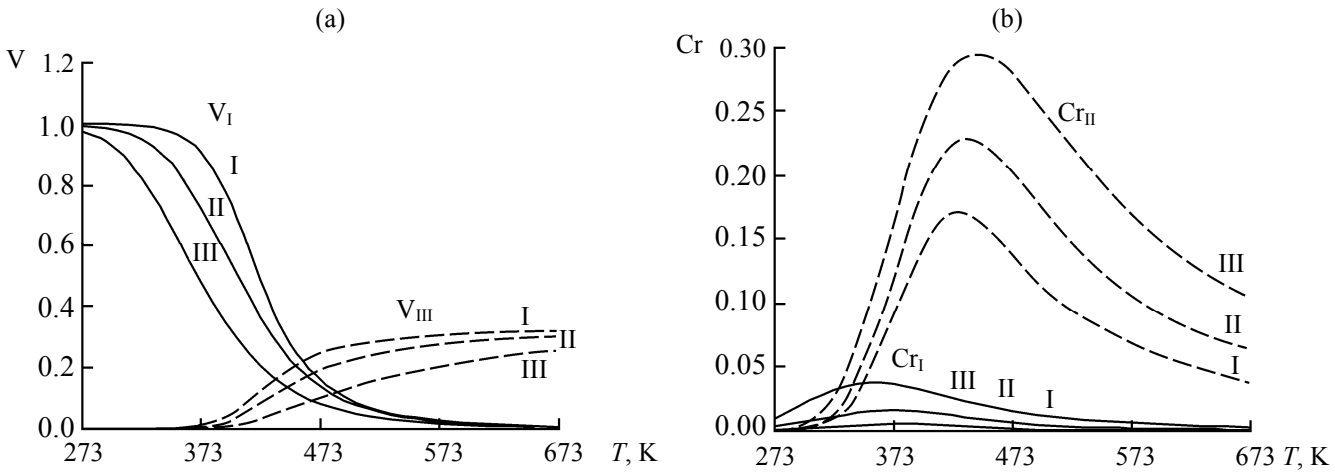

Fig. 5. Calculated content of element-oxide centers of various functionality vs. temperature, at the following values of energy of the structural strain: 95, 70 and 23 kJ mol^{-1} for the centers of V_{III}, V_{II}, and Cr_{II} respectively: (a) vanadium containing centers and (b) chromium containing centers.

stretching vibrations are masked by strong absorption of the silica substrate in the region of 1000–1200 cm^{-1}, therefore for the identification first of all may serve the peaks of Si–O–E stretching vibrations. For the asymmetric Si–O–Cr vibrations in the bidentate groups, in the IR spectra absorption bands at 910–920 cm^{-1} are expected, and similar peak in the range of 930–940 cm^{-1} is expected for the three-functional vanadium-containing centers, and in the region of 950–970 cm^{-1} should be expected a band of the Si–O–Cr and Si–OV stretching vibrations in monodentate structures.

Experimental FTIR spectra of the samples (Fig. 6) contain absorption bands in the area of 910 cm^{-1}, which are absent in the spectrum of the initial silica gel. Their intensity is in line with the content of chromium in the samples. According to the calculations, this band, with a high degree of reliability, can be attributed to the asymmetric stretching vibrations of Si–O–Cr in the bidentate groups. The intensity of the weakly expressed peaks in the region of 950–960 cm^{-1} shows no apparent dependence on the concentration of chromium or vanadium. Based on the calculated predictions, we can assume that they correspond to Si–O–V and Si–O–Cr vibrations in the monodentate structures. The band of asymmetric vibration Si–O–V in polydentate groups is expected at 930–940 cm^{-1}. These bands may also contribute to the broad band in the region of 950 cm^{-1}. These results correlate with previously obtained data. For example, in [4, 22] the spectral peaks at 940 and 960 cm^{-1} were attributed to the Si–O–V vibrations, and the peaks at 910 and 960 cm^{-1}, to Si–O–Cr. Consequently, the results of spectroscopic studies on a semi-quantitative level agree with the calculated prediction of the normal vibrations for the coatings composition corresponding to Fig. 4.

Table 2. Estimated frequencies of vibration modes of vanadium- and chromium-containing groups on the silica surface, cm^{-1}, E is the modifying element.

Model	Vibration mode frequency, cm^{-1}			
	ν_sE–Cl/ν_{as}E–Cl		ν_sSi–O–E/ν_{as}Si–O–E	
	harmonic approximation	taking into account anharmonicity	harmonic approximation	taking into account anharmonicity
Cr_I	491	486	971	950
CR_{II}	–	–	980/925	965/918
V_I	500/447	496/446	976	954
V_{II}	465	461	996/950	977/933
V_{III}	–	–	995/941	993/926

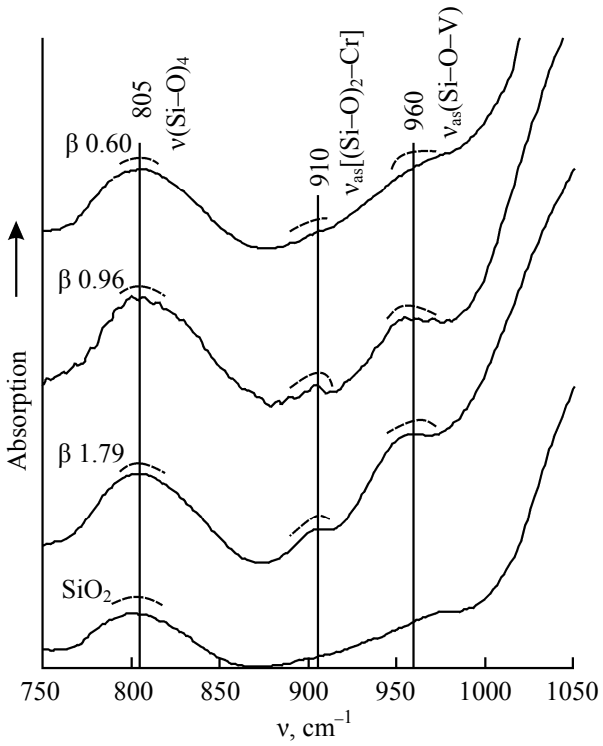

Fig. 6. Fourier IR spectra of parent silica and the synthesized samples with different values of β.

Thus, we carried out experimental synthesis of binary vanadium–chromium-containing coatings on the surface of silica by processing the latter with a mixture of vapor of $VOCl_3$ and CrO_2Cl_2. The developped method of quantum-chemical modeling of the products of such synthesis can be used to identify the structure of local centers, and to predict the composition of the coating. The achieved consistence of the calculated and experimental data allows a priori selection of the optimal concentration and temperature conditions of synthesis, providing meaningful regulation of the product composition.

The developed method can be applied also at the synthesis of other multi-component systems on the silica surface.

EXPERIMENTAL

The quantum-chemical calculations were performed with the program GAUSSIAN®03W [23] using density functional theory B3LYP [24] and the atomic orbital basis set 6-31G** [25] in accordance with the method of [14]. Modeling the local structure of the modified silica surface was carried out in the framework of the cluster approach. Hydrogen atoms were used as pseudoatoms. To estimate the effect of structural strains the SiO_2 surface cluster models of different sizes were compared: the minimal with a single silicon atom (H_3SiOH) (Figs. 2a, 2b) and those built on the basis of section (111) of β-cristobalite [14], containing 10 atoms Si and three OH groups (Figs. 2c, 2d).

Structure of each model was optimized with high accuracy, and the total energy of interaction of nuclei and electrons and the energy of vibration states in the harmonic approximation were calculated. On this basis, the absolute values of standard Gibbs free energy of all reactants and possible products of chemical reactions at a given temperature were determined. For the gas phase components, using the known relations of statistical thermodynamics, the contributions of translational, rotational and vibrational motion were taken into account in the approximations of an ideal gas, rigid rotor and harmonic oscillator, respectively. For the surface sites a model of hard cluster [26] was used which includes only the vibrational motion of atoms. The configuration entropy of the modified surfaces was considered in the approximation of the ideal two-dimensional lattice solution.

The calculation of equilibrium concentrations was carried out by the method of finding extremes of the characteristic functions [27] for the isobaric-isothermal closed system in the framework of the dual Lagrange problem with the elemental balance of vanadium, chromium, silicon and oxygen.

The anharmonic vibrational effects were estimated using second-order perturbation theory [28].

Synthesis of two-component coatings was carried out in gas-phase flow system in accordance with the known method [6–8] at a constant temperature 200±5°C. The silica gel of ShSKG grade (S_{sp} = 250 $m^2 g^{-1}$; [OH] = 2.6 mmol g^{-1}) was used as a carrier, the sources of the modifying elements were vanadium oxychloride ($VOCl_3$, chemically pure grade) and chromium oxychloride (CrO_2Cl_2, the product of the laboratory synthesis). Quantitative determination of vanadium and chromium in the reaction products and in the gas phase was carried out by transferring into solution and the subsequent photocolorimetric analysis with hydrogen peroxide [29] and diphenylcarbazide [30], respectively.

Registration of the FTIR transmission spectra was carried out on a FSM-1201 spectrometer in the spectral

range from 400 to 1400 cm^{-1} with a resolution of 1 cm^{-1}. The test samples were pressed into pellets with KBr.

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