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Structure of the Products of $TiCl_4$ Chemisorption on the Surface of Porous Silica in the Process of Vapor-Phase Hydrolysis

E. A. Sosnov, A. A. Malkov, and A. A. Malygin

St. Petersburg State Technological Institute, Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: sosnov@lti-gti.ru

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Abstract—Changes in coordination environment of titanium atoms in the composition of the titanium oxychloride groups chemisorbed on the surface of porous silica after the vapor-phase hydrolysis are considered. It is shown that after the substitution of chlorine atoms by the OH groups, additional coordination bonds between the titanium-containing group and neighboring hydroxo groups are formed, that leads to an increase to 6 in the coordination number of titanium in the composition of the surface polyhedra.

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For the synthesis of titanium oxide structures on the surface of silica using consecutive cyclic reactions of titanium tetrachloride and water with hydroxyl groups of the silica source was described in quite a number of publications [1–13]. However, a detailed analysis of the relevant publications shows that they mostly deal with the aspects of chemical transformations taking place at the interaction of matrix with low-molecular reagents. However, in view of the tetrahedral structure of the $TiCl_4$ molecule and octahedral environments characteristic of titanium atoms in oxides [14], it is important to understand the processes that take place at the phase transition on the surface during the formation of titanium oxide structures in the cyclic synthesis. We have considered previously the influence of temperature of thermal preparation of the silica matrix and of the chemisorption of $TiCl_4$ on the coordination state of titanium in the composition of titanium oxychloride groups [15].

In this paper we consider a change in coordination environment of titanium atoms in the chemisorbed titanium oxychloride structures in the course of vapor phase hydrolysis.

The results of chemical analytical studies of the products obtained are shown in Table 1. A comparison of the presented results with the chemical composition of the initial titanium oxychloride groups [16] allows us to conclude that the number of titanium-containing groups on the surface of porous silica after the hydrolysis does not change, regardless of the temperature of hydrolysis T_H. At the same time, using IR spectroscopy it has been previously shown [7] that in the course of the vapor-phase hydrolysis the anchor links in some of the titanium oxychloride groups monofunctionally (n = 1) connected with the matrix surface can be broken, whereas the bonds $(\equiv Si–O)_n–TiCl_{4–n}$ of polyfunctionally connected groups (n = 2–3) are hydrolytically stable [7, 17].

Thus, the competition of two processes is possible at the vapor-phase hydrolysis: the substitution of chlorine atoms in the titanium oxychloride groups by OH groups, and hydrolytic rupture of single Si–O–Ti bonds. Depending on the ratio of the rates of these reaction, they can lead to different results.

If the substitution proceeds first (this is more likely, because the chlorine atoms are located above the surface of the carrier [18] and are readily accessible, have a high electronegativity and chemical activity), two successive processes will occur:

$$(\equiv Si–O–)_nTiCl_{4–n} + H_2O \rightarrow (\equiv Si–O–)_nTi(OH)_{4–n} + HCl, \quad (1)$$
$$1 \le n \le 3;$$

$$\equiv Si–O–Ti(OH)_3 + H_2O \rightarrow \equiv Si–OH + Ti(OH)_4\downarrow. \quad (2)$$

The formed titanium hydroxide can again interact with closely spaced silanols located on the matrix surface, with the regeneration of Si–O–Ti bonds.

Table 1. Chemical composition of titanium-containing structures after vapor-phase hydrolysis

$T_{CS} = T_H$, °C	T_O, °C						
	200	300	400	500	600	700	800
200	1.09 2.39[a] 0.32	1.03 2.34 0.24	1.02 2.36 0.15	0.91 1.99 0.10	0.73 1.63 0.08	0.49 1.20 0.08	0.35 0.93 0.08
300		0.90 1.86 0.18	0.85 1.70 0.09	0.80 1.55 0.04	0.58 1.12 0.04	0.42 0.95 0.05	0.30 0.74 0.04
400			0.76 1.37 0.00	0.69 1.19 0.00	0.49 0.88 0.00	0.37 0.72 0.00	0.29 0.66 0.00
500				0.63 1.06 0.00	0.50 0.88 0.00	0.37 0.74 0.00	0.28 0.65 0.00
600					0.49 0.88 0.00	0.38 0.71 0.00	0.28 0.67 0.00
700						0.38 0.89 0.00	0.28 0.69 0.00
800							0.28 0.64 0.00

[a] Content, mmol/g_0, [Ti] [Cl_Σ] = [Cl_H] + [Cl_{SP}]/[$Cl_{\underline{SP}}$] (SP means solid phase).

Otherwise, if hydrolysis of Si–O–Ti bond proceeds more actively, then reaction (3) [17, 19] should proceed leading to the release into the gas phase of volatile titanium hydroxychloride, which in the flow system will be partially removed from the reaction zone, reducing the amount of titanium-containing structures on the matrix surface. The possibility of such a process is found by quantum-chemical calculations of isolated clusters [20], but the probability of its occurrence (ΔE = 36 kJ mol^{-1} per a chemical bond), as compared with the reaction of Cl-substitution group (ΔE = –34 kJ mol^{-1}), is extremely small.

$$(\equiv Si–O–)TiCl_3 + H_2O \rightarrow \equiv Si–OH + Ti(OH)Cl_3\uparrow. \qquad (3)$$

After hydrolysis of titanium oxychloride groups in any conditions (regardless of the temperature conditions of their synthesis in the range of 200–800°C), no titanium was registered in the composition of the trapped low molecular reaction products, and these products removed from the reaction zone contain only the chlorine atoms, which indicates that under these conditions the reaction proceeds along the first mechanism [reactions (1) and (2)].

However, at carrying out hydrolysis at T_H below 300°C the complete replacement of chlorine atoms by hydroxo groups has not been achieved even in a prolonged (up to 10 h) process (Table 1). (Similar results were observed previously at the vapor-phase hydrolysis of titanium oxychloride groups, deposited at 180°C on glasses [21] and at 150°C on silica [22].) The increase in the concentration of water vapor in the reaction medium from 20 to 250 g m^{-3} has not changed the degree of chlorine substitution in solid-phase products of the synthesis. At higher T_H chlorine was not found in the solid products of the reaction.

Inasmuch as the titanium oxychloride structures are capable to form additional coordination bonds with closely spaced hydroxy groups not reacted with $TiCl_4$ thus increasing the titanium coordination number (CN_{Ti}) in the titanium-containing surface polyhedron [15], we can assume that the observed effect of the process temperature on the degree of substitution of Cl groups is defined by the non-uniformity of the latter caused by the participation of some of the chlorine atoms in the coordination bonds.

To determine the coordination state of titanium in the formed titanium–hydroxyl structures, we obtained electron diffuse reflectance spectra (DRS) of the samples synthesized under the conditions of equal temperatures of thermal treatment of initial matrix, chemisorption and hydrolysis, $T_O = T_{CS} = T_H$ = 200, 400, 600, and 800°C. Chemical composition of the

Table 2. Chemical composition of the groups on the surface of silica gel ShSKG after the chemisorption of $TiCl_4$ and subsequent hydrolysis

$T_O = T_{CS} = T_H$, °C	Silica gel ShSKG		Titanium oxychloride groups			Titanium hydroxide groups		
	content of $[OH]_{init}$, mmol/g_0 [23]	d_{OH-OH}, nm[a]	content of [Ti], mmol/g_0	[Cl]/[Ti]	contents $[OH]_{residual}$[a], mmol/g_0	content, mmol/g_0		
						[Ti]	$[Cl]_{solid\ phase}$	$[OH]_{Ti}$[b]
200	3.57	1.28	1.08	2.17	1.58	1.08	0.32	2.07
400	2.51	1.49	0.79	1.70	0.69	0.79	0.00	1.37
600	1.67	1.81	0.49	1.65	0.51	0.49	0.00	0.88
800	0.86	2.49	0.28	2.29	0.38	0.28	0.00	0.64

[a] Calculated value. [b] Calculated value without accounting for the reduction in the number of OH groups due to the condensation with the formation of Ti–O–Ti bonds.

samples is given in Table 2. The DRS spectra were registered before and after the vapor-phase hydrolysis (Fig. 1).

Changes in the chemical environment of titanium atoms (substitution of Cl groups by OH groups after hydrolysis) lead to the shift of DRS absorption band to longer wavelengths, while the maximum value of the reflectivity of the samples remains practically unchanged. Comparison of the changes in the DRS spectra with changes in the chemical composition of titanium-containing surface structures shows that two opposite factors affect the position of the fundamental absorption band:

(1) The replacement of the chlorine atoms belonging to titanium oxychloride group by OH groups. It is known that in the molecular structures in the series of TiI_4, $TiBr_4$, and $TiCl_4$ a decrease in the ligand mass shifts the maximum of absorption band to shorter wavelengths: ν_{max} = 19 600 cm^{-1} (510 nm), 27750–29500 cm^{-1} (339–360 nm), and 34840–35600 cm^{-1}

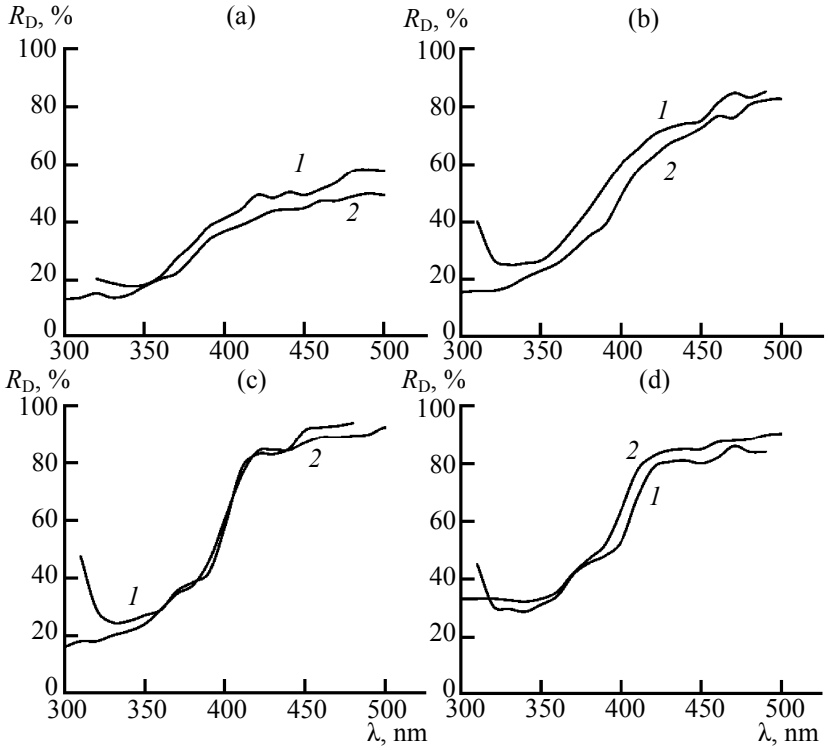


Fig. 1. DRS spectra of (*1*) titanium oxychloride and (*2*) titanium hydroxide structures on the surface of silica ShSKG. Synthesis at temperature, ºC: (a) 200, (b) 400, (c) 600, and (d) 800.

(281–287 nm), respectively [24–26]. A replacement of one of the Cl atoms by CH_3 group that is close in mass to hydroxy group, is also accompanied by a shift of the maximum absorption band to a value of 43 000 cm^{-1} (233 nm) [24].

In this case we consider the spectra of single molecules with a broad absorption band in the optical spectrum, that is characterized by the position of its maximum. In the charge-transfer spectra characteristic of solid phase materials, at the formation of cluster structure of the size more than 10^5 atoms [27] a quasi-continuous spectrum of energy band is observed, which can only be characterized by the edge of the absorption band (Fig. 2). The observed difference at the determination of positions of the maxima of molecular and cluster systems is just a result of the different characterization of the spectral bands.

(2) Increase in CN_{Ti} above 4, that is typical first of all for monofunctionally bound titanium oxychloride groups without formed additional coordination bonds with closely spaced hydroxy groups of the initial matrix [15], to 6. Similar processes in molecular systems lead to a shift of the absorption band maximum to longer wavelengths: for $TiCl_4$ the position of the maximum is 34840–35600 cm^{-1} (281–287 nm), and for $[TiCl_6]^{2-}$ it is 25 000 cm^{-1} (400 nm) [25]. At the same time with the increase in CN_{Ti} the energy of the Ti–Cl bond is reduced (and the bond length, respectively, increases), because a repulsion between the ligands is also manifested [25].

The increase in CN_{Ti} may be caused by several processes:

– The physical sorption of water molecules (or molecular oxygen) on the titanium-hydroxy groups with the formation of structures (4);

– The migration of the protons of the hydroxy groups of the original matrix [28] and the formation of coordination bonds with the grafted groups, similar to that established for the titanium oxychloride structures [15] [scheme (5)]. This process can be stipulated by the presence of excess water vapor, capable of rehydroxylation of strained siloxane bridges on the surface of the matrix [29], although according to [30–32] the rehydroxylation is slow;

– The formation of coordination bonds with hydroxy groups of closely spaced titanium hydroxide fragments [scheme (6)];

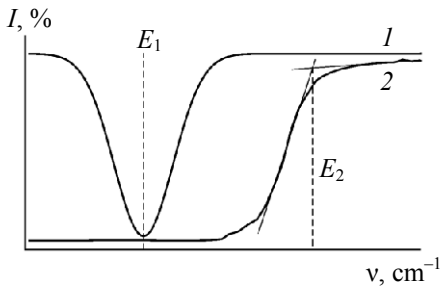
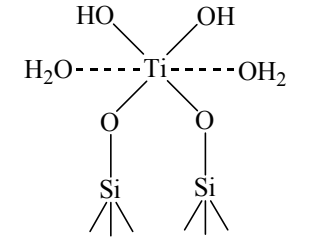
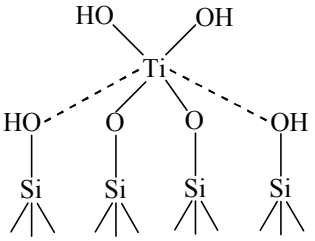


Fig. 2. Schematic pattern of the optical spectrum of the (*1*) molecular system and (*2*) solid-phase material.

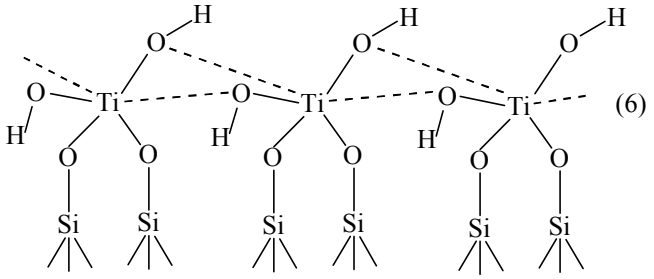
– In the case of reaction (2) leading to the formation of $Ti(OH)_4$ on the surface of the carrier, titanium hydroxide can agglomerate and lose water turning into a microcrystallites of TiO_2, where titanium has CN_{Ti} = 6 [33].



(4)



(5)



(6)

It should be noted, however, that among the above considered processes leading to an increase in CN_{Ti}, the first one is not typical for the processes carried out at high T_H, taking into account that the removal of the physically sorbed water from the TiO_2 surface occurs at 75–120°C, and the coordinationally bound water, at 140–240°C [33].

Assuming that like observed earlier [15] for titanium oxychloride groups, on the surface of the matrix

Table 3. Results of mathematical resolution of the bands in the DRS spectra

$T_O = T_{CS} = T_H$, °C	Characteristics of the bands in the DRS spectra											
	after chemisorption						after hydrolysis					
	1st band			2nd band			1st band			2nd band		
	λ_1, nm	E_1, eV	I_1, %	λ_2, nm	E_2, eV	I_2, %	λ_1, nm	E_1, eV	I_1, %	λ_2, nm	E_2, eV	I_2, %
200	344	3.61	9	387	3.20	91	368	3.37	36	397	3.12	64
400	346	3.58	18	405	3.06	82	369	3.36	39	399	3.10	61
600	362	3.43	34	402	3.08	66	364	3.41	24	402	3.09	76
800	369	3.36	27	403	3.08	73	366	3.39	39	408	3.04	61

also may be present titanium-containing structures with different coordination environments we resolved the spectra obtained into components described by the Fermi–Dirac distribution according to the procedure in [34]. The results of mathematical processing of the spectra are shown in Table 3. Comparing the results of mathematical processing of DRS spectra of titanium oxychloride and titanium hydroxide structures, we should note the following.

After the chemisorption of $TiCl_4$ on the ShSKG silica gel surface 2 type of the titanium oxychloride structures are formed differing by coordination environments of the central atom: with $CN_{Ti} = 4$ and 6. Upon increase in temperature T_{CS} an increase is observed in the intensity of the band corresponding to the tetrahedral coordination of titanium (λ ~345 nm) and a gradual shift of its position to 370 nm. This phenomenon may be caused by gradual tuning of surface silicon oxide tetrahedra that leads both to an increase in symmetry of the titanium oxychloride groups, and increase of CN_{Ti} over 4.

Replacing the chlorine atom by the lighter OH group should lead to a shift of the band in the DRS spectrum to shorter wavelengths, but this effect is not observed. Apparently, a change in the spectra is a result of other effects: in addition to the change of the ligand an increase in CN_{Ti} occurs due to the formation of additional coordination bonds by the schemes (4)–(6).

The surface of dispersed silica by the local structure is close to the faces (111) and (110) of β-cristobalite [35] with periodic arrangement of hydroxy groups. Despite the fact that the average distance between the attached groups with increase in T_O (the increase in degree of dehydroxylation of the matrix surface) increases from 1.3 nm at 200°C to 2.5 nm at 800°C (Table 2), the actual distance between the groups should remain virtually unchanged, since the process of dehydroxylation is not uniform, and is of the local nature [36, 37]. Indeed, upon the decrease in the size of a spot of the matrix with hydroxy groups, the more chemisorbed titanium oxychloride structures are tends to be arranged at its border, and in the absence of nearby OH groups they remain with $CN_{Ti} = 4$. (However, the increase of T_{CS} can significantly increase the conformational mobility of the chemisorbed groups and the surface $[SiO_4]$ tetrahedra, which leads to some leveling of the bond lengths in titanium oxychloride groups and allows the CN_{Ti} to raise through coordination bonding with the neighboring titanium-containing structures.)

After hydrolysis, from the DRS spectra disappear the bands characteristic of tetrahedrally coordinated titanium (λ = 340–350 nm [38]) and only the structures remain with the octahedral coordination of the titanium of different symmetry. Thus, a unification occurs of titanium oxide structures: ~35–40% have anatase-like structure (where few Ti–O bonds are longer than the others), and 60–65% of structures with more aligned bonds, with the coordination of titanium atoms close to the state of Ti atoms in rutile. This is also evidenced by the characteristic energy spectra of charge transfer, close to the band gap of these titanium oxides (Table 3).

This result may indicate that, regardless of whether a $TiCl_4$ molecule chemisorbed on the surface of silica succeeded or failed to form additional bonds with neighboring hydroxy groups, after the vapor-phase hydrolysis these bonds are formed (not necessarily with silanols: to improve coordination the hydroxy groups may be involved bound to neighboring titanium atoms).

EXPERIMENTAL

Titanium oxychloride groups synthesized on the surface of silica gel of wide-porous brand ShSKG in the temperature range of the preliminary heat treatment of the matrix (T_O) and the chemisorption (T_{CS}) 200–800°C [39], the spatial structure of which is discussed in [15], were subjected to vapor-phase hydrolysis in a flow system under conditions of continuous removal of low molecular weight reaction products [40] at temperatures (T_H) same as at chemisorption of $TiCl_4$.

Gaseous low molecular weight reaction products were trapped at the outlet of the reactor and, together with the obtained solid-phase products were analyzed on the content of titanium [1, 41] and chlorine [42]. To compare the chemical composition of the surface groups formed under different thermal conditions, the contents of elements were assigned to 1 g of anhydrous silica (g_0) [1, 43]. The electronic spectra of diffuse reflection (DRS) were registered in the wavelength range 300 – 1000 nm in the spectrophotometric unit equipped with air-tight optical cell [38], which allows the study without any contact with the atmosphere. As an optical standard was used Aerosil A-300 calcined at 600°C.

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