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Hydrolytic stability of the Si – O – Ti bonds in the chemical assembly of titania nanostructures on silica surfaces

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Abstract. The hydrolytic stability of the Si – O – Ti bonds in titania nanostructures on the surface of silica materials of different genesis is analyzed. The mechanism of hydrolysis is considered and the decisive role of structural and chemical features of silicas in the stability of titania nanostructures on their surface is demonstrated. The bibliography includes 193 references.

I. Introduction

Chemical modification of solid surfaces is widely used for developing functional structures on them.

A method of molecular layering developed by Aleskovskii and Kol'tsov [1 – 6] in the 1960s for the chemical assembly of element-oxide nanostructures using volatile chlorides and water vapour as the reagents involves the iteration of the following four physicochemical steps:

1) interaction of the halide with surface sites of the solid-state matrix, *i.e.*, the chemisorption step;

2) removal of the excess of the non-consumed low-molecular starting reagent and volatile reaction products, *i.e.*, the desorption step that follows chemisorption;

3) treatment of chlorine-containing products with water vapour, *i.e.*, the vapour-phase hydrolysis step;

4) removal of excess water vapour and volatile reaction products, *i.e.*, the desorption step that follows the vapour-phase hydrolysis.

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Moreover, steps 1 and 3 should be carried out as far from equilibrium as possible (to remove gaseous products as completely as possible from the reaction zone) and steps 2 and 4 should proceed up to complete removal of low-molecular starting reagents and volatile reaction products physically adsorbed on the solid matrix surface from the reaction zone.[6]

The approach to the formation of element-oxide and other structures on the surface, proposed by Aleskovskii, is widely studied both in Russia and abroad. In many publications, in place of the term 'molecular layering', other names were used for this synthetic method, such as atomic layer epitaxy (ALE), atomic layer deposition (ALD), *etc.*[7] In essence, these processes largely match the molecular lamination principles described by Aleskovskii and Kol'tsov.

The largest number of publications in this field are devoted to studies of chemical transformations in different steps of chemical assembly of titania structures on the surface of different forms of silica. These reactions have been studied for about five decades.[1, 6, 8 – 13] It can be noted that the silica – titania nanolayer system has become a sort of classical structure not only of purely scientific interest but also of practical importance for the development of materials of different functional purposes (catalyst, sorbents, pigments, luminophores, composites, *etc.*). However, so far, the publications by different authors often contain ambiguous and inconsistent interpretations of experimental data on the mechanism of interface formation in the system solid matrix – growing titania nanostructures in different steps of synthesis.[2, 5, 14 – 31]

II. Chemisorption of titanium compounds

The first step of the synthesis, *viz.*, the chemisorption of $TiCl_4$ vapour on the surface of different silicas, has been discussed in detail in studies by Aleskovskii, Kol'tsov and their successors (see Refs 1 – 6, 14, 18, 32 – 41) including those carried out in the past two decades (see Refs 9, 17, 20,

22, 24, 42–49) and also in publications by other scientists from different countries (Refs 8, 10, 11, 15, 16, 19, 21, 23, 27, 29, 50–92). It was almost generally agreed that in a certain temperature interval, the primary step of chemisorption on the silica surface preferentially occurred on the hydroxyl groups to form $TiCl_x$ groups bound to the support by one, two or three bonds ($x = 3$, 2 or 1, respectively) (from here on, $\equiv Si-$ designates Si atoms on the silica surface):

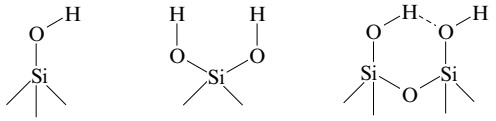
$$\equiv Si{-}OH + TiCl_4 \longrightarrow \equiv Si{-}O{-}TiCl_3 + HCl, \quad (1)$$

$$\begin{matrix}\equiv Si{-}OH \\ \equiv Si{-}OH\end{matrix} + TiCl_4 \longrightarrow \begin{matrix}\equiv Si{-}O \\ \equiv Si{-}O\end{matrix}\!\!>TiCl_2 + 2\,HCl, \quad (2)$$

$$\begin{matrix}\equiv Si{-}OH \\ \equiv Si{-}OH \\ \equiv Si{-}OH\end{matrix} + TiCl_4 \longrightarrow \begin{matrix}\equiv Si{-}O \\ \equiv Si{-}O \\ \equiv Si{-}O\end{matrix}\!\!>TiCl + 3\,HCl. \quad (3)$$

The ratio between different $TiCl_x$ groups determined in the majority of cases from the Cl : Ti ratio depended on the technological prehistory of used silica, the degree of its dehydroxylation and the temperature in the chemisorption step.[4, 8, 14, 58, 59, 76]

Reactions with titanium tetrachloride could involve isolated (or terminal) (**1**), geminal (**2**) and vicinal (**3**) OH groups of silica.



1 **2** **3**

A part of them do not react with the halide being shielded by chemisorbed groups[14, 49, 59] and can form coordination bonds with the $TiCl_x$ structures fixed on the silica surface thus increasing the coordination number of titanium (CN_{Ti}) to 5–6.[49]

The possibility of nucleophilic interaction between $TiCl_4$ and the strained $Si-O-Si$ bonds on the surface of dehydroxylated silica was reported;[54, 75, 84, 93] this included cleavage of the $Si-O-Si$ bond and the direct chlorination of the surface.

$$\begin{matrix}\equiv Si \\ \equiv Si\end{matrix}\!\!>O + TiCl_4 \longrightarrow \equiv Si{-}O{-}TiCl_3 + \equiv Si{-}Cl. \quad (4)$$

At the same time, the siloxane bonds were assumed[94, 95] to be non-reactive in surface chemical reactions. Moreover, it was shown[96] that process (4) does not proceed even after the surface dehydroxylation at 600 °C. The terminal silanol groups on the SiO_2 surface were protected by the reaction with hexamethyldisilazane [$(Me_3Si)_2NH$], the geminal and vicinal groups were removed by dehydroxylation of silica at 600 °C. After the subsequent treatment with $TiCl_4$ vapour even at 600 °C, no significant amounts of titanium were observed on the support surface.

The second step of chemical assembly of superficial titania structure, *i.e.*, the removal of the excess of $TiCl_4$ together with the gaseous reaction product (HCl), is a purely physical process and its efficiency requires that it followed the peculiarities of the conditions of synthesis[45] with consideration of the diffusion limitations arising in pores of the matrix used.

In catalysis, chlorine-free active titanium-containing structures on the support surface are often obtained by a slightly modified method of chemical assembly. Thus the chemisorption of titanium alkoxides $Ti(OPr^i)_4$,[97–101] $TiCl_2(OPr^i)_2$,[97] $Ti(OBu^n)_4$[102–106] was carried out from solutions in anhydrous ethanol,[98, 102, 106] butanol,[104] toluene,[97, 100, 101, 104] n-hexane[99, 105, 107] or cyclohexane[103] followed by repeated washing of the modified matrix with a solvent of the same series to remove the excess of adsorbate that did not react and the reaction by-products that formed. No substantial difference was observed as compared with reactions (1)–(3); hence, the process can be described by the following equation:

$$(4-x)\equiv Si{-}OH + Ti(OR)_4 \longrightarrow (\equiv Si{-}O)_{4-x}Ti(OR)_x + (4-x)\,ROH.$$

III. Hydrolysis of titanium oxychloride groups

Many publications were devoted to experimental studies of the third step of chemical assembly (hydrolysis of titanium oxychloride or titanium alkoxide structures (Refs 2, 5, 14–28, 30, 107 and 108); however, the interpretations given in different publications often substantially differed. Thus both the stoichiometric substitution of OH groups for chlorine atoms by the reaction

$$(\equiv Si{-}O)_{4-x}TiCl_x + x\,H_2O \longrightarrow (\equiv Si{-}O)_{4-x}Ti(OH)_x + x\,HCl, \quad (5)$$

and conversely the complete cleavage of chemical bonds between the chemisorbed titanium-containing groups and the matrix surface (hydrolysis of $Si-O-Ti$ bonds) to form the TiO_2 phase and hydrogen chloride can be mentioned.

$$(\equiv Si{-}O)_{4-x}TiCl_x + 2\,H_2O \longrightarrow (4-x)\equiv Si{-}OH + TiO_2 + x\,HCl.$$

The estimates of hydrolytic stability of the $Si-O-Ti$ bond were also controversial varying in different studies from 'very stable'[109] to 'hydrolytically unstable' and 'readily hydrolyzable even at room temperature'.[67, 68, 110] At the same time, it should be noted that the mentioned step of synthesis is important from the viewpoint of surface pretreatment before the subsequent secondary treatment of modified silica with titanium tetrachloride vapour aimed at the formation of the second element oxide monolayer.

Considering the problem of hydrolytic stability of the $Si-O-Ti$ bond, mention should be made of two approaches, thermodynamic and kinetic, to solve this problem.

Unfortunately, the thermodynamic aspects of the chemical reaction on the surface of nanostructured highly dispersed materials remain virtually non-studied. Recently, certain studies have been devoted to the general principles of thermodynamics of nanomaterials,[111] and several studies dealt with quantum chemical simulation of titanium tetrachloride chemisorption[112, 113] and the $Si-O-Ti$ bond hydrolysis.[113, 114] However, the absence of experimental data on the thermodynamics of elementary steps of the process[115] as well as substantial drawbacks of quantum chemical simulation methods used so far (the limited possibilities of calculations in the absence of translation symme-

try in the structural organization of the silica matrix surface layer;[116] the effect of the size of modelled cluster and of the type and the mass of univalent pseudoatoms used for binding the cluster on the quality of quantum chemical models;[113] the considerable effect of both the atomic orbital basis set chosen for computations and the computation method;[117, 118] the emergence of strong anharmonic effects upon the introduction of a d-element into the structure of the simulated cluster[118]) results in a substantial scatter of the results of quantum chemical simulations.[118] Thus, only comparative data on the change in characteristics of objects with similar chemical nature could be obtained.[113]

Taking into account the aforementioned factors and bearing in mind that it is kinetics of processes that is the subject of a large number of publications, in the present review attention was focused on the analysis of data on hydrolytic stability of chemisorbed $TiCl_x$ groups and on the structure of titanium-oxide groups formed on the surface of wide-pore silica gel upon vapour-phase hydrolysis.

IV. Certain characteristics of titanium-containing silica specimens

A series of studies devoted to the targeted synthesis of solid nanostructured materials including the formation of the silica core–titania nanoshell system were carried out at the Department of Chemical Nanotechnology and Electronic Engineering Materials of the St Petersburg State Technological Institute. In these studies, wide-pore ShSKG silica gel with the specific surface (S_{sp}) of 246 $m^2\ g^{-1}$ and the specific pore volume (V_p) of 0.96 $cm^3\ g^{-1}$ was used. The chemical assembly of titanium-containing structures was accomplished in a flow-through system[45] in the temperature range of 200–800 °C. The real stoichiometric ratios were obtained by recalculating the contents of titanium, chlorine and OH groups in samples per g of anhydrous silica (designated as g_0).[4, 47] In special experiments, a flow-through quartz reactor of an original design was used, which was combined with an optical cell for the *in situ* IR spectroscopic studies of the samples (Fig. 1).[42] The accuracy of sample positioning in the cell was ±0.5 mm along the rod axis and ±1° with respect to the plane of optical windows. IR Spectra were recorded using an IKS-29 spectrometer in the double-beam transmission mode.

The processes that occur during the vapour-phase hydrolysis of titanium oxychloride groups on the surface of disperse silica were investigated using the samples prepared in two different temperature modes. In the first mode,

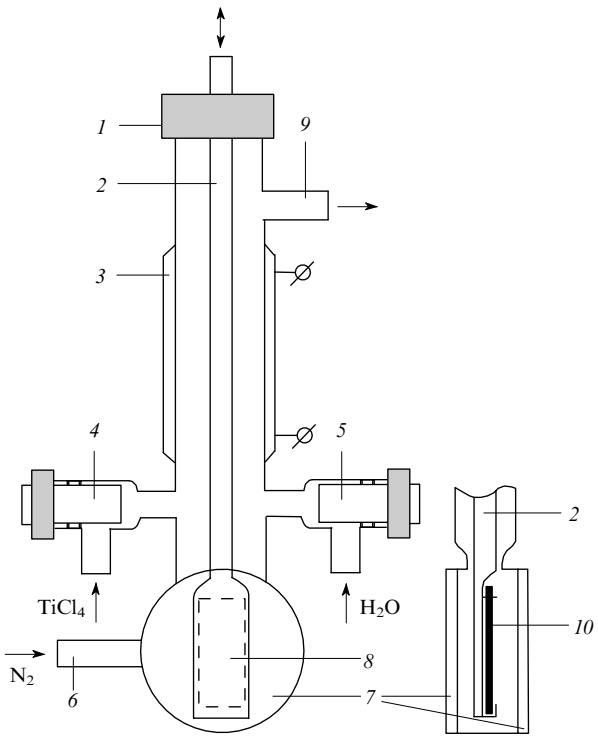


Figure 1. Cell for *in situ* IR spectroscopic studies combined with the reactor.
(*1*) sealing unit, (*2*) rod with a sample holder, (*3*) resistance furnace, (*4*) pipe for supplying $TiCl_4$ with an isolating valve, (*5*) pipe for supplying H_2O with an isolating valve, (*6*) pipe for supplying the carrier gas, (*7*) optical windows (KBr), (*8*) orifice in the holder, (*9*) gas outlet, (*10*) sample.

all steps of synthesis were carried out at a constant temperature, *i.e.*, $T_o = T_{chs} = T_h = T_t$ (T_o, T_{chs}, T_h, T_t are the temperatures of dehydroxylation, chemisorption, vapour-phase hydrolysis and thermal treatment, respectively) (Table 1, samples 1–3). Samples of the second type were subjected to dehydroxylation under more drastic conditions (T_o = 800 °C) and then titanium oxychloride structures were synthesized at different temperatures in each step. Comparing the results obtained for samples of these two types allowed several conclusions on the mechanism of hydrolysis of titanium oxychloride groups on the silica surface to be drawn.

Table 1. The effect of temperature on the chemical composition of titanium-containing groups formed on the silica gel surface.

Sample	Temperature of synthesis steps /°C				Ti content /mmol g_0^{-1}	Ratio [Cl] : [Ti]
	T_o	T_{chs}	T_h	T_t		
1	200	200	200	200	1.08	2.17
2	400	400	400	400	0.79	1.70
3	600	600	600	600	0.49	1.65
4	800	200	200	200 → 1200	0.35	2.65
5	800	400	25 → 400	400 → 800	0.29	2.29
6	800	600	200 → 600	600 → 800	0.28	2.41
7	800	800	200 → 800	800	0.28	2.29
8	600	200 → 600	200	200	0.37	1.98

V. IR spectroscopic studies

IR spectroscopy is a highly informative method that allows one to assess the processes occurring on interfaces; hence, it is widely used in studying vapour-phase hydrolysis of titanium oxychloride groups on the surface of disperse silica. When all steps of synthesis were carried out at a constant temperature, $(\equiv Si-O)_{4-x}TiCl_x$ groups with $x < 3$ on average formed. According to spectroscopic data, additional coordination bonds of a part of titanium-containing structures are established with closely located silanol groups that remaimed intact. This increased the coordination number of titanium atom to 5–6.[49]

Figure 2 shows the IR spectra of samples 1–3 (see Table 1) measured before and after vapour-phase hydrolysis. Upon chemisorption of $TiCl_4$, the spectra of products (curves *2* in Fig. 2) demonstrated substantially weaker absorption in the range of 3500–3750 cm^{-1} pertaining to different forms of hydroxy groups [both the terminal groups that had a pronounced absorption band (AB) with the maximum at 3744–3750 cm^{-1} (Refs 11, 31, 71, 74) and the hydrogen-bonded groups that exhibited several broad overlapping AB in the vicinity of 3500–3700 cm^{-1} (Ref. 71)]. At the same time, the spectra of all samples contained a shoulder-shaped absorption band in the vicinity of 910–920 cm^{-1} [in differential spectra, the maximum of this absorption band was observed at 896–906 cm^{-1} (curves *2′* in Fig. 2)], which can be attributed to asymmetric vibrations of the Si–O–Ti bonds formed in reactions (1)–(3), and broad bands in the frequency ranges of 650–700 cm^{-1} (Refs 30, 84, 100, 105, 119–122) and 720–780 cm^{-1} (Refs 85, 99, 119, 123, 124), respectively. The mentioned spectral regions of the manifestation of the AB pertained to vibrations of the Ti–O bonds with different coordination environment of titanium. The coordination polyhedron with 4 oxygen atoms ($CN_{Ti} = 4$) is characterized by a band at 720–780 cm^{-1}, while the polyhedron with $CN_{Ti} = 6$ demonstrated a band at 650–700 cm^{-1} (Refs 100, 119). It should be noted that as the average multiplicity of Si–O–Ti anchor bonds [determined as 4 — ([Cl]:[Ti])] increased from 1.83 at 200 °C to 2.35 at 600 °C, the AB maximum shifted to lower frequencies (from 906 to 896 cm^{-1}).

Following the shifts of AB assigned to the formation of the Si–O–Ti bond in spectra of pyrogenic silicas (aerosils) and $TiCl_4$-vapour-modified silica gels dehydroxylated at $T_o > 200$ °C allowed two types of titanium oxychloride structures formed on the matrix to be distinguished, namely, the groups bound to the surface with one (AB 990–1030 cm^{-1}) and two bonds (920–930 cm^{-1}) (Refs 11, 30, 31, 73, 74, 84, 85, 96, 125). In this case, the titanium atom had tetrahedral environment.[30, 73, 74]

Many authors observed the absorption band in the vicinity of 940–960 cm^{-1} attributed to the Si–O–Ti structural fragment in titanium–silica systems synthesized by the sol–gel method (Refs 25, 98, 100–102, 105, 107, 109, 121, 122, 126–140) or 930–940 cm^{-1}.[63, 141–149] Certain authors[122, 126, 144, 146] stressed that titanium atoms involved in the Si–O–Ti bond had the tetrahedral coordination. However, other authors observed AB maxima in lower positions (expressed in cm^{-1}): 920–940,[150] 920,[75, 110, 151, 152] 919–925,[2] 900–930,[153] 900[119, 154] and even at 890.[150] Moreover, the appearance of a band at 900 cm^{-1} was explained[119] by the increase in CN_{Ti} to 5.

The same spectral range (950–980 cm^{-1}) contained an absorption band corresponding to asymmetrical stretching vibrations ν_{Si-O} of the terminal Si–[OH] fragments.[155] At the same time, many authors who have observed the Si–O–Ti stretching bands at 940–960 cm^{-1} either totally ignored the presence of the band that corresponded to the Si–[OH] (silanol group) vibrations or pointed to the complex nature of the detected AB. Thus, it was emphasized that these two closely located spectral bands cannot be separated.

However, the presence and the intensity of this band could have a substantial effect on the observed absorption peak position and the band shape. Thus it was shown[156] that for titania–silica systems synthesized by the sol–gel method, a wide AB with the maximum at 969 cm^{-1} corresponding to the freshly formed titania–silica sol changed its shape and shifted to 924 cm^{-1} upon gelation accompanied by the loss of its 'hydroxyl coating' and further to 920 cm^{-1} upon calcination of titania–silica at 900 °C. The similar shift of the band to the low-frequency range (from 928 to 900 cm^{-1}) was observed[99] during the thermal treatment of mesoporous silica SBA-15 modified with titanium.

The procedure of separation of bands corresponding to vibrations of Si–O–Ti and Si–[OH] bonds was proposed[135] based on the assumption of proportionality of the intensities of bands for the hydroxyl groups in the ranges of 3590 and 960 cm^{-1}. However, the use of IR spectra in the Gurevich–Kubelka–Munk coordinates brought about distortions into the real peak maxima and intensities for the spectral bands to be separated.[157] Moreover, the fact that in these calculations the intensities of absorption bands only for the hydrogen-bonded hydroxy groups (3500–3700 cm^{-1}) were taken into account wheras the bands of terminal silanol groups (3744–3750 cm^{-1})[11, 31, 71, 74] were ignored also introduced substantial error into the obtained results.

Yet another procedure for separation was the spectrum deconvolution into the constituent spectral bands. Thus approximation of absorption bands by the Gauss distribution for the complex AB observed at 935 cm^{-1} made it possible to distinguish two components at 980 and 930 cm^{-1}, which were attributed to the vibrations of Si–[OH] and Si–O–Ti bonds, respectively.[147]

The simplest method that allowed establishment of the real positions of individual spectral bands and their intensities in the course of chemical reactions consisted of measuring differential spectra *in situ*. This method allowed location of the real position of AB peaks including those manifested as shoulders of complex bands (Refs 11, 31, 71, 74, 84, 85, 99, 108).

Thus, the position of the peak of an absorption band corresponding to the formation of Si–O–Ti anchor bonds made it possible to judge on the coordination environment of the atom-modifier and the multiplicity of its bond with the matrix surface, while the changes in the band intensity make it possible to judge on the stability of titanium oxychloride groups formed in the course of synthesis. The latter assumption can be used in assessing the hydrolytic stability of the Si–O–Ti bond.

As follows from dependences shown in Fig. 2, for samples 1–3, the vapour-phase hydrolysis was accompanied by the following changes in IR spectra.

1. The AB of terminal hydroxy groups were partly restored; however, this involved the shift of the band maximum of newly appeared hydroxy groups to

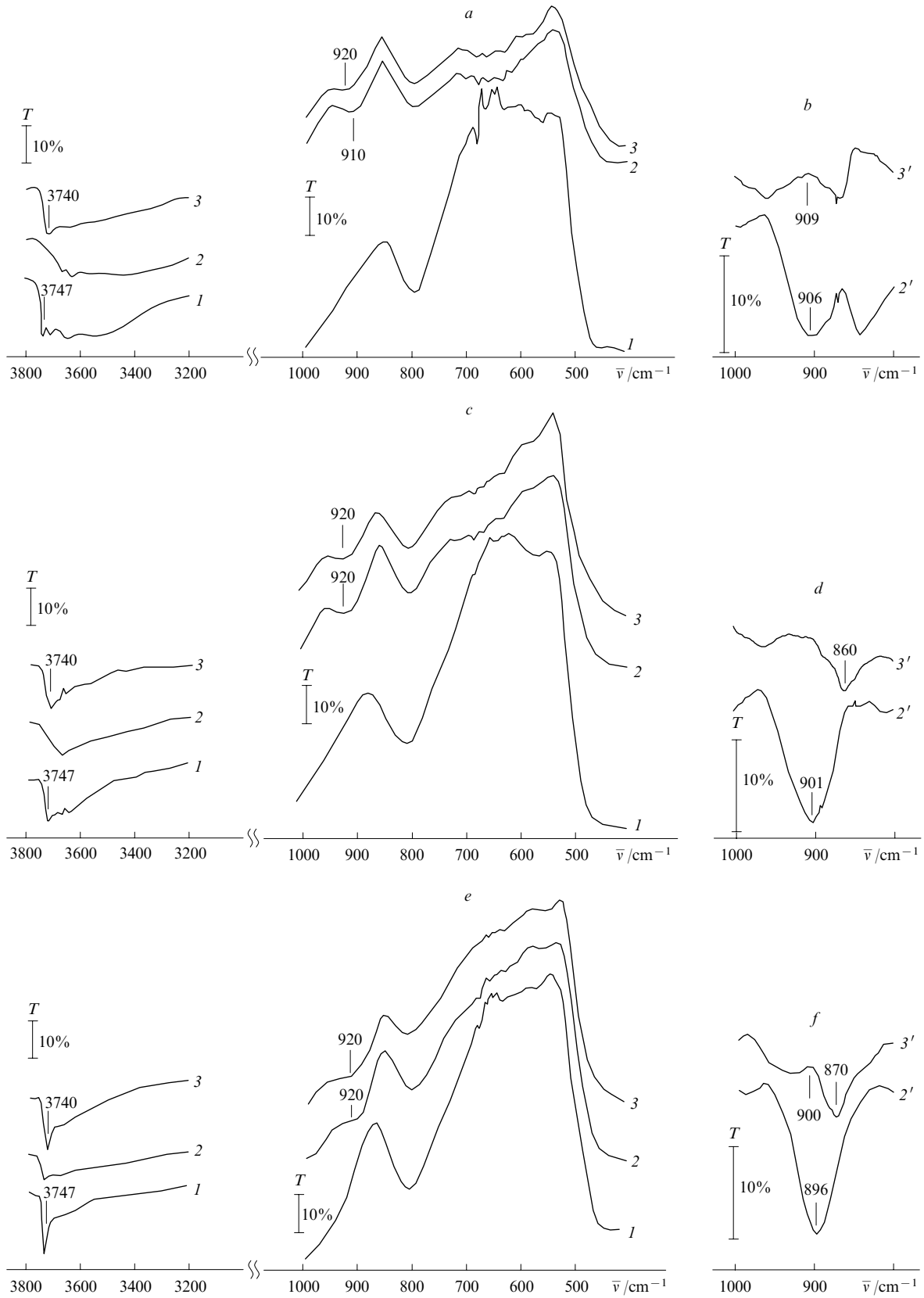


Figure 2. IR spectra, *in situ* (*a*, *c*, *e*) and differential (*b*, *d*, *f*), of silica gel samples modified at different temperatures.
$T_o = T_{chs} = T_h = T_t = 200$ (*a*, *b*), 400 (*c*, *d*), 600 °C (*e*, *f*). (*1*) original silica gel after thermal treatment; (*2*, *2′*) after $TiCl_4$ chemisorption; (*3*, *3′*) after vapour-phase hydrolysis. From hereon, *n′* are differential spectra obtained by subtraction of the preliminary curve from a given spectrum (for example, *2′* is the result of *2*—*1* subtraction).

3730 – 3740 cm^{-1}; this may suggest that OH groups were bound not with the silicon atoms of the matrix but with titanium atoms as the result of exchange of chloride ions in titanium oxychloride groups.[158]

2. Virtually no changes in the spectral region corresponding to the absorption of the Si – O – Ti bond (900 – 950 cm^{-1}) were observed (curves *2*, *3* in Fig. 2). Only the differential spectrum of sample 1 (Fig. 2 *a*, curve *3′*) demonstrated an insignificant (by ~10%) decrease in the AB intensity for the Si – O – Ti bond, which could be caused by its cleavage in ≡Si – O – $TiCl_3$ groups during hydrolysis.[22,24]

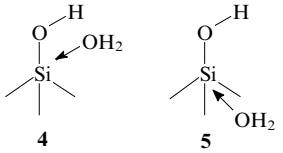
3. In the vicinity of 700 – 800 cm^{-1}, the absorption bands with maxima at 860 and 880 cm^{-1} appeared in differential spectra (curves *3′* in Fig. 2), and their intensities increased with the increase in hydrolysis temperature. In line with the previously considered trend of the band shift to low frequencies with the increase in the titanium coordination number, the appearance of AB in this spectral region could be associated with the increase in CN_{Ti} to 6, which is typical of TiO_2 crystalline phases. The increase in CN was apparently associated with the increased mobility of hydroxy groups and grafted fragments and could occur both as a result of formation of additional coordination bonds between silanol groups that remained uninvolved in chemisorption and hydrolyzed titanium oxychloride groups[49] and as a result of formation of coordination bonds between the newly appeared Ti – OH groups and adjacent (at a distance no larger than two Ti – O bond lengths) titanium-containing groups.

These results (first of all, the stability of the absorption band intensity for the corresponding Si – O – Ti bonds in samples containing titanium oxychloride groups bound with the support by two or three bonds [curves *3*, *3′* in Fig. 2 *c*–*f*)] suggest that such surface structures exhibit hydrolytic stability under vapour-phase hydrolysis conditions even at 600 °C. Analogous results were obtained earlier in studies of the vapour-phase hydrolysis of titanium oxychloride groups formed in the temperature range of 25 – 200 °C on silica gel samples dehydroxylated at T_o = 600 °C.[22,24]

VI. Hydrolytic stability of the titanium oxychloride groups on silicas

The hydrolytic stability of titanium oxychloride groups with bonds of different multiplicity formed between an individual group and the support surface was investigated for the titanium oxychloride structures synthesized at different temperatures (samples 4 – 7 in Table 1). Figures 3 – 6 show the IR spectra of the products synthesized in a reactor combined with a cell.

The preliminary thermal treatment of silica at 800 °C made it possible to remove not only all the types of coordinatively bound water [both located on the material surface (structure **4**) and incorporated through hexagonal voids into the near-surface SiO_2 layer (structure **5**)]



4 **5**

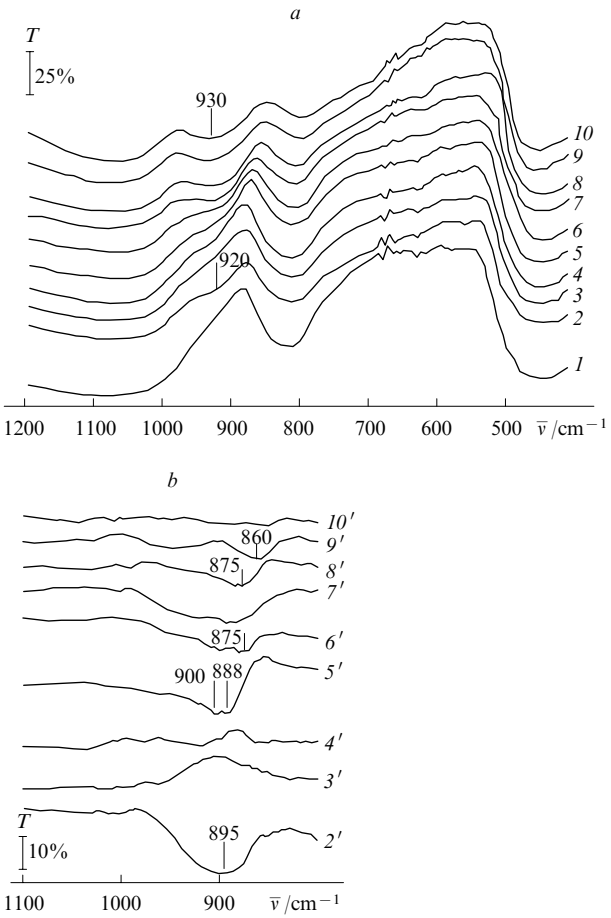


Figure 3. IR spectra, *in situ* (*a*) and differential (*b*), of sample 4 in the following steps of synthesis: after thermal treatment of the original silica gel (*1*), after $TiCl_4$ chemisorption (*2*), after vapour-phase hydrolysis (*3*), after further thermal treatment at 400 (*4*), 600 (*5*), 800 (*6*), 900 (*7*), 1000 (*8*), 1100 (*9*) and 1200 °C (*10*).

but also geminal and vicinal silanol groups (structures **2**, **3**). This was accompanied by the following changes in the IR spectra: an increase in the transmission ability of silica in the region of 850 – 1000 cm^{-1} and virtually complete disappearance of an AB with the maximum at 980 cm^{-1} (see Fig. 6 *a*, curves *1*, *2*). At the same time, the differential spectrum (see Fig. 6 *b*, curve 2′) evidenced of an increase in the intensity for a band corresponding to Si – [OH] fragments probably due to the liberation of hydroxy groups earlier hydrogen-bonded physically adsorbed water (a broad asymmetric band at 850 – 950 cm^{-1}).

Following treatment of the support with $TiCl_4$ vapour as for samples discussed earlier (see Fig. 2), for all T_{chs}, a shoulder-shaped AB appeared in the IR spectra at 910 – 920 cm^{-1} (curves *2* in Fig. 3 *a*, 4 *a*, 5 *a*, curve *3* in Fig. 6 *a*). The differential spectra made it possible to determine the position of the maximum of this band in vicinity of 895 – 910 cm^{-1}. With the increase in T_{chs}, the AB peak shifted to higher frequencies, which could evidence of a decrease in CN_{Ti} in titanium oxychloride structures[30,73,74,119] (*i.e.*, the decrease in the number of coordination bonds between the element-modifier and intact silanol groups). Moreover, as follows from the chemical analysis data (see Table 1), for all T_{chs} the composition of titanium oxychloride structures formed on silica dehydroxy-

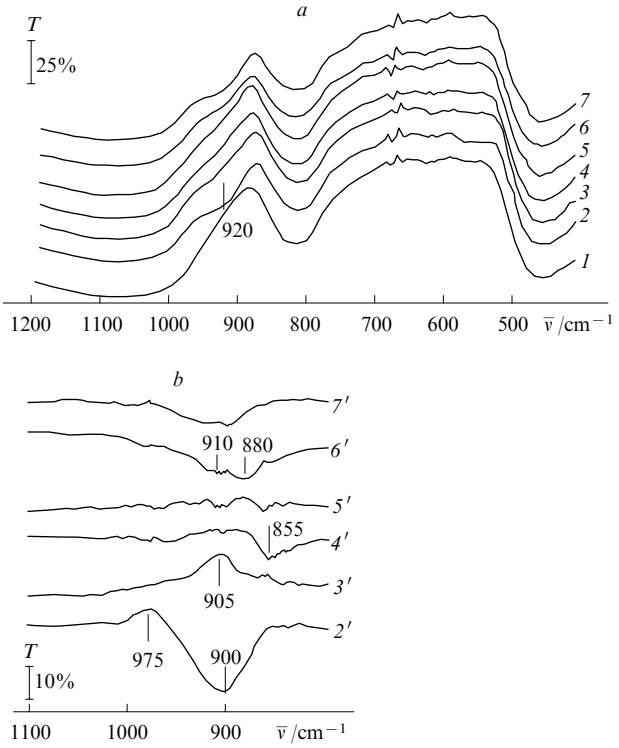


Figure 4. IR spectra, *in situ* (*a*) and differential (*b*), of sample 5 in the following steps of synthesis: after thermal treatment of the original silica gel (*1*), after $TiCl_4$ chemisorption (*2*), after vapour-phase hydrolysis at 25 (*3*), 200 (*4*) and 400 °C (*5*), after further thermal treatment at 600 (*6*) and 800 °C (*7*).

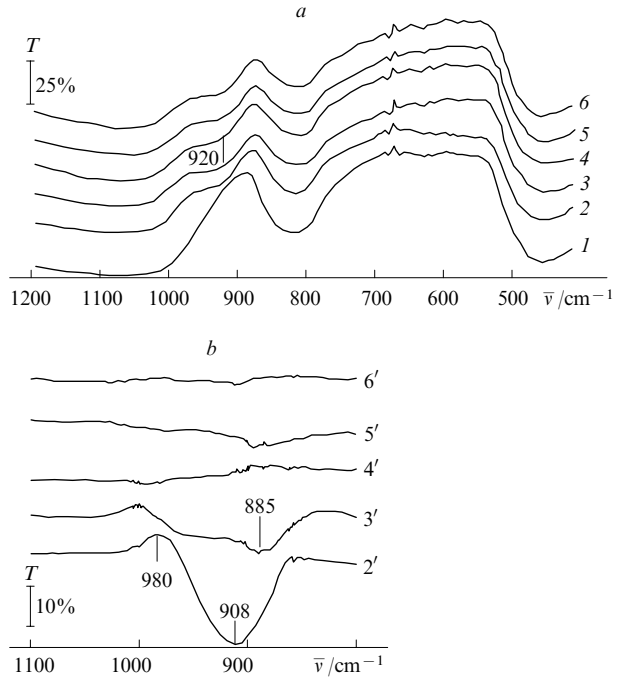


Figure 5. IR spectra, *in situ* (*a*) and differential (*b*), of sample 6 in the following steps of synthesis: after thermal treatment of the original silica gel (*1*), after $TiCl_4$ chemisorption (*2*), after vapour-phase hydrolysis at 200 (*3*), 400 (*4*) and 600 °C (*5*), after further thermal treatment at 800 °C (*6*).

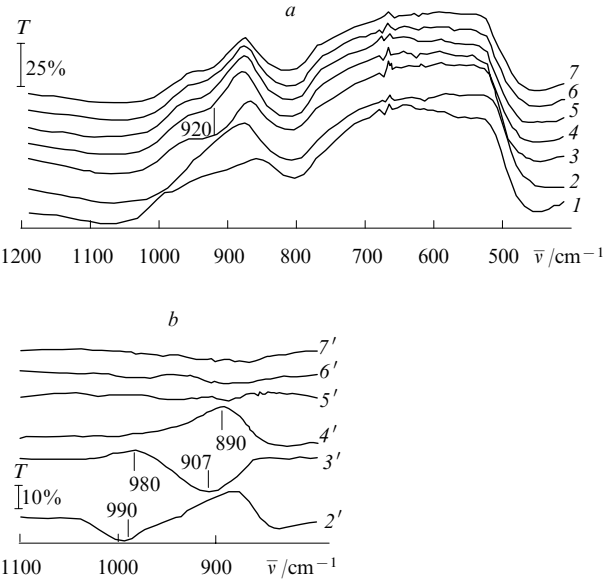


Figure 6. IR spectra, *in situ* (*a*) and differential (*b*), of sample 7 in the following steps of synthesis: air-dry silica gel (*1*), silica gel after thermal treatment (*2*), after $TiCl_4$ chemisorption (*3*), after vapour-phase hydrolysis at 200 (*4*), 400 (*5*), 600 (*6*) and 800 °C (*7*).

lated at 800 °C insignificantly differed both quantitatively (0.35 – 0.28 mmol g_0^{-1}) and qualitatively (in all cases, only groups bound with the surface by one or two bonds formed and, under the assumption of uniform distribution of chemisorbed groups over the matrix surface, the distance between them was 1.08 – 1.21 nm for T_{chs} = 200 – 800 °C).

The vapour-phase hydrolysis of samples was carried out at temperatures not exceeding that of $TiCl_4$ chemisorption. The limitation on T_h was associated with the fact that heating of silicas containing chemisorbed $TiCl_x$ groups above the T_{chs} temperature led to disproportionation between titanium-containing structures to evolve $TiCl_4$ into the gas phase and an increase in the multiplicity of the bond formed by an individual group with the support surface.[48, 76]

Vapour-phase hydrolysis of samples obtained following the $TiCl_4$ chemisorption at different T_{chs} reduced the intensity of the band corresponding to the Si—O—Ti bond by 25% – 30% (see Figs 3, 4). These spectral changes pointed to the decrease in the number of anchor bonds formed by titanium-containing groups, *i.e.*, in the course of hydrolysis a part of Si—O—Ti bonds were broken. Simultaneously, the maximum of the mentioned band shifted to higher frequencies, which was probably associated with the ligand substitution in the titanium-containing group (replacement of the Cl atom by the lighter OH group).

The increase in the reactor temperature from 200 to 400 °C (irrespective of the presence of water vapour in the gas phase) did not bring about any changes in the intensity of the absorption band of the Si—O—Ti bond, which pointed to the absence of secondary interactions between the titanium hydroxide structures formed in the course of hydrolysis and the functional groups of disperse silica. It should be noted that after a part of Si—O—Ti bonds were broken at the temperature $\leqslant$ 200 °C, the condensation of detached $Ti(OH)_4$ fragments occurred simultaneously with the hydrolysis to afford titania species, which was accom-

panied by the appearance of an IR band with the maximum at 860 cm typical of Ti—O—Ti bonds. This process was revealed by analyzing changes in the spectra when the first step of hydrolysis was carried out at room temperature (curves *3*, *3′* in Fig. 4) and then T_h was increased to 200 °C (curves *4*, *4′* in Fig. 4).

The further rise of the temperature in this system to 600–800 °C led to insignificant (by ~8%–10%) recovery of Si—O—Ti bonds. This process could be observed up to temperatures of ~1100 °C, where the changes in the absorption band intensity for the Si—O—Ti bond could still be distinguished. The further temperature rise caused no changes in the spectra.

The recovery of the Si—O—Ti bond can be attributed to quite a number of competitive processes:

— interaction of grafted hydroxyl titanium groups with protons from silanol groups that remained free after the $TiCl_4$ chemisorption and could migrate over the dehydroxylated silica surface;[159,160]

— interaction of earlier detached $Ti(OH)_4$ species with hydroxy groups of silica;[68]

— direct reaction between dehydroxylated SiO_2 and TiO_2 to afford solid solutions.[120,161–163]

To estimate the contributions of mentioned interactions into the overall surface transformations, special experiments were carried out. On the surface of silica gel dehydroxylated at 600 °C, chemisorption of $TiCl_4$ was carried out at 200 °C. The resulting samples with titanium oxychloride groups were subjected to thermal treatment in an inert gas flow as the temperature was elevated to 600 °C. Then, at the same temperature, the treatment with water vapour was carried out (sample 8 in Table 1). Figure 7 shows the IR spectra after different steps of synthesis.

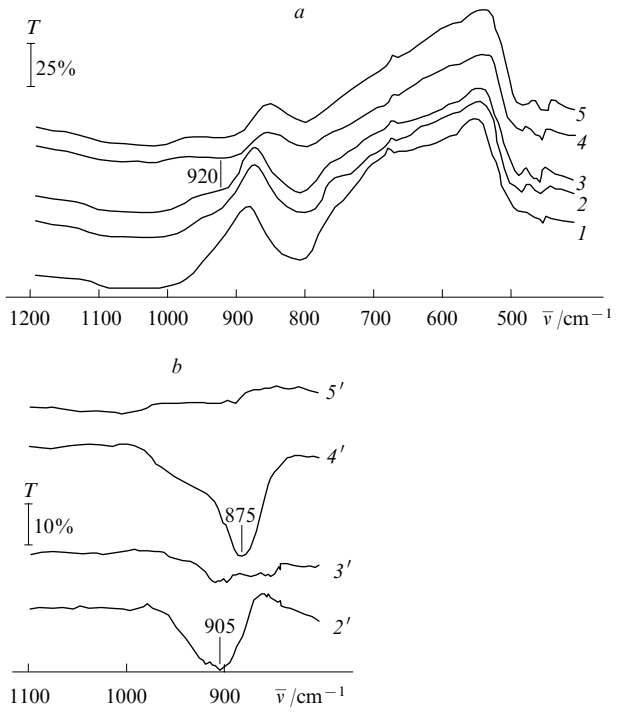


Figure 7. IR spectra, *in situ* (*a*) and differential (*b*), of sample 8 in the following stages of synthesis: after thermal treatment of the original silica gel (*1*), after $TiCl_4$ chemisorption at 200 (*2*), 400 (*3*) and 600 °C (*4*), after vapour-phase hydrolysis at 600 °C (*5*).

The thermal treatment of $TiCl_x$ groups is known to be accompanied by disproportionation to increase the multiplicity of the bond between an individual titanium oxychloride group and the matrix surface and evolve $TiCl_4$ into the gas phase.[48,76] However, according to analytical studies and calculations, such processes could not change the total number of bonds of titanium oxychloride groups with the silicon support surface (*i.e.*, the total number of Si—O—Ti bonds). Hence, it can be assumed that the increase in the absorption band intensity observed for the Si—O—Ti bond in the IR spectra was associated with an increase in the degree of connectivity of an individual $TiCl_x$ group due to its interaction with the silanol groups that did not react earlier with $TiCl_4$. Judging from the appearance of two AB with maxima at 890 and 950 cm^{-1} in the differential spectra, the Si—O—Ti bonds form preferentially with titanium atoms with $CN_{Ti} = 6$. This assumption was confirmed by the data of electron spectroscopy of diffuse reflectance (ESDR).[49] The same was evidenced by the absence of changes in the intensity of the Si—O—Ti band after vapour-phase hydrolysis (curve *5′* in Fig. 7 *b*), because under these conditions only titanium oxychloride structures bound with the surface by multiple bonds were present on the silica surface. According to experimental data, these groups were hydrolytically stable.

Thus, the recovery of the absorption band corresponding to the Si—O—Ti bond observed in the IR spectra (see Figs 3–6) in the range of 600–800 °C can be attributed to the interaction of silanol groups that remained intact in $TiCl_4$ chemisorption with the grafted hydroxy titanium groups. At higher temperatures (up to 1100 °C), titanium atoms could diffuse into the superficial silica layer.[161–163]

Similar data indicating the hydrolytic stability of the Si—O—Ti bond under conditions of synthesis were obtained in many studies.[2,5,15,18,26,30] However, certain research groups stated that the water-vapour treatment could break the Si—O—Ti bond under milder temperature conditions (*i.e.*, substantially below 600 °C).

Thus, for highly dispersed pyrogenic silica modified at 150 °C in the reaction with $TiCl_4$ (aerosil A-300, $S_{sp} = 270$ m^2 g^{-1}), the water-vapour treatment carried out under static conditions at 150 °C was accompanied by the complete cleavage of Si—O—Ti anchor bonds, which presumably precluded the formation of the titania coating chemically bound with the support.[16,23] The reason for the observed phenomenon was associated with violation of the following fundamental principle of chemical assembling by molecular layering: in the discussed studies, the working process was not carried out as far as possible from equilibrium,[6] but was performed under static conditions where hydrogen chloride [the reaction (5) product] was not removed but, in contrast, was accumulated in the reaction zone; this favoured the secondary reactions between HCl and titanium-containing groups[164] and the disproportionation of titanium hydroxychlorides.

$$(\equiv Si{-}O)_{4-x}Ti(OH)_x + HCl \longrightarrow$$
$$\longrightarrow \equiv Si{-}OH + Ti(OH)_xCl_{4-x} \longrightarrow$$
$$\longrightarrow \equiv Si{-}OH + TiO_2 + HCl + H_2O.$$

However, the very fact of total cleavage of the Si—O—Ti bonds requires explanation.

It was inferred by Finnish scientists in studies of the ADL synthesis of titania coatings on the surface of different

silicas [silicate glasses,[10] EP-10 silica (S_{sp} = 300 $m^2\ g^{-1}$, V_p = 1.75 $cm^3\ g^{-1}$),[77,81] *etc.*] in a vacuum system that the Si—O—Ti bonds were resistant to water vapour at the reaction temperature of $\leqslant$ 250 °C, whereas at higher temperatures ($\geqslant$ 300 °C) hydrolytic abstraction of titanium hydroxychlorides [$Ti(OH)_{4-x}Cl_x$] volatile under these conditions occurred which was followed by their disproportionation to TiO_2 and $TiCl_4$.[165]

$$(\equiv Si{-}O)_{4-x}TiCl_x + H_2O \longrightarrow \equiv Si{-}OH + Ti(OH)_{4-x}Cl_x \longrightarrow \equiv Si{-}OH + TiO_2 + TiCl_4 + H_2O.$$

Certain scientists[29,166,167] studied the ADL synthesis of titania coatings with different starting titanium compounds [$TiCl_4$,[29] $Ti(OEt)_4$,[166] $Ti(OPr^i)_4$ (Ref. 167)] in a low-pressure (250 Pa) flow-through system; however, they did not focus attention on the hydrolytic stability of the Si—O—Ti bond. At the same time, they assumed that titanium-containing structures chemisorbed on the matrix surface at 100–350 °C could break their anchor bonds and migrate over the matrix surface to form TiO_2 agglomerates. However, as follows from the analysis of the above results, it is possible that certain methodical conditions of the synthesis were ignored in these experiments. Thus titania films synthesized at T < 150 °C from $Ti(OEt)_4$ contained considerable amounts of carbon,[166] originating probably from titanium alkoxides. Possibly, the low-molecular-weight reagents and the reaction products were incompletely removed during the desorption steps, as evidenced by the sample mass gain during the vapour phase hydrolysis,[29] which was associated with either the adsorption of water vapour on the sample surface or with the characteristic gas-phase deposition of TiO_2 as the result of reaction between the titanium-containing reagent and water vapour. Moreover, the use of titanium alkoxides as the reagents in gas-phase reactions at temperatures above 200 °C was unreasonable due to their thermal instability.[168]

At the same time, it should be noted that as follows from some data,[108] the use of $Ti(OPr^i)_4$ and H_2O and the fulfilment of the temperature–time conditions of the synthesis led to the formation of titania monolayers with the Si—O—Ti bonds of high hydrolytic stability.

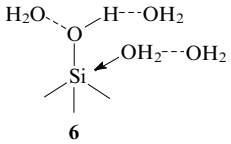
The effect of the ALD process conditions on the hydrolytic stability of the Si—O—Ti bond was shown in an IR spectroscopic study[31] of the products of this synthesis, which was carried out in the temperature range of 25–300 °C. The reaction of $TiCl_4$ vapour with A-300 aerosil was carried out in a vacuum system (reagent delivery at 10^5 Pa, evacuation at 1 Pa for 5 min). Throughout the temperature range chosen, the halide chemisorption was accompanied by the appearance, in the IR spectra, of absorption bands corresponding to the Si—O—Ti bonds involved in the $\equiv Si{-}O{-}TiCl_3$ and $(\equiv Si{-}O)_2TiCl_2$ structures, where the AB intensity substantially depended on the temperature. After the vapour-phase hydrolysis at 25 °C, when the IR spectra demonstrated the appearance of a broad band at 3350–3400 cm^{-1} and a band at 1610 cm^{-1}, which corresponded to water molecules adsorbed on the support surface, the break of Si—O—Ti bonds was observed. Although, advancing the ideas of the Finnish scientists (*vide supra*), it was assumed that hydrolysis involved the detachment of $Ti(OH)_{4-x}Cl_x$ molecules, the absence of chemical analysis data on the reaction products made impossible unambiguous identification of the chemical environment of titanium in the structure detached from the matrix. With the increase in the number of treatment cycles (to 4), the amount of adsorbed water and the degree of cleavage of the Si—O—Ti bonds progressively increased. At T = 300 °C, when no H_2O adsorption was observed on the SiO_2 surface, the anchor bonds remained stable even after 4 cycles of synthesis.

The liquid-phase hydrolysis of titanium-containing structures fixed on the surface of porous silica supports was also accompanied by the partial cleavage of the Si—O—Ti bonds. However, their complete destruction could be observed neither during the treatment of titania–silicas synthesized by the sol–gel technology by the co-hydrolysis of alkoxy compounds,[123,169–171] nor in the hydrolysis of grafted titanium-containing structures. In one of studies it was shown[28] that only approximately the half of chemisorbed titanium atoms was observed to pass to solution upon the liquid-phase hydrolysis of titanium oxychloride groups fixed on the surface of highly porous MSM-41 silica (S_{sp} = 1071 $m^2\ g^{-1}$, V_p = 2.13 $cm^3\ g^{-1}$).

Carrying out liquid-phase hydrolysis in acidic media [in the presence of 0.1 M HNO_3 (Ref. 104) or HCl (Ref. 172)] substantially increased the rate of Si—O—Ti bond hydrolysis and its efficiency. Under such conditions, the liquid-phase treatment of titanium oxychloride groups chemisorbed on silica supports led to virtually complete destruction of the Si—O—Ti bonds and the deposition of TiO_2 within the support pores.[25] In addition, the long-term effect of liquid water at high temperatures (4 h at 97 °C) favoured the hydrothermal formation of TiO_2 in the anatase modification.[173]

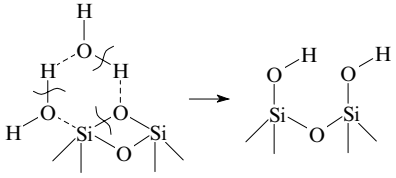
VII. Mechanism of water interaction with the Si—O—Ti bond

The reason for such a radical difference in the results obtained by different groups of scientists can be found if we consider the mechanism of water interaction with the surface of dehydroxylated silica. It was shown[174–181] that water molecules are adsorbed on hydroxyl groups according to, first of all, the coordination mechanism (structures **4**, **5**) and then through hydrogen bonding (structure **6**).



6

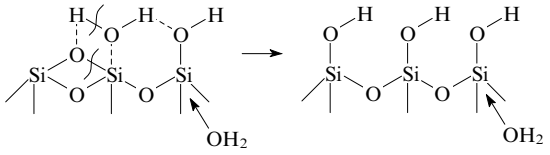
The latter structures, being fixed loosely on the silica surface, can interact with the adjacent strained Si—O—Si bridges to form the six-centred transition structure (bonds to be broken are crossed with wavy lines).[182]



(6)

However, because water is preferentially adsorbed by hydroxyl groups (as indicated by hydrophobicity of completely dehydroxylated silica surface[183]) and, taking into

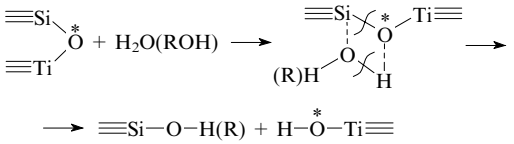
account the 'islet' mechanism of rehydroxylation,[184] the rehydroxylation scheme that involves silanol groups as the 'catalysts' seems most probable.



Vapour-phase rehydroxylation of SiO_2 proceeded extremely slowly and only strongly dehydroxylated silicas could be rehydroxylated even if partly by liquid water only.[185–187] Complete recovery of the hydroxyl coating of silicas calcined at 600–1000 °C could be achieved only after their boiling in water for 60 h.[188]

The replacement of one silicon atom in the strained siloxane bridge by a titanium atom, which is less electronegative than silicon (according to Pauling, their electronegativities are 1.54 and 1.90, respectively), should result in asymmetry of the bridging oxygen atom and enhance the reactivity of the strained bridging. The higher activity of the Si–O–Ti bond as compared with Si–O–Si follows from the data[65] that confirmed the migration of molecules of physically adsorbed water over the surface of pyrogenic titanium–silicas from Si–O–Si to Si–O–Ti groups during the dehydration. Thus, the interaction of the Si–O–Ti bond with H_2O, which is analogous to the siloxane rehydroxylation, reaction should occur under milder conditions.

Studies of the mechanism of hydrolysis of the Si–O–Ti bond carried out by ^{17}O NMR spectroscopy have shown[123] that the interaction started with incorporation of H_2O or ROH molecules into the coordination sphere of silicon atoms and proceeded by the mechanism of nucleophilic substitution (S_N) to afford a transition complex, which was followed by cleavage of the Si–O bond.

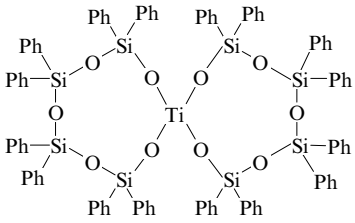


The higher reactivity of the Si–O bond in the Si–O–Ti fragment was attested by calculations of the potential energy distribution over the Si–O–Ti bridge structures (72% and 28% for Si–O and Ti–O, respectively) carried out by molecular dynamics methods.[146]

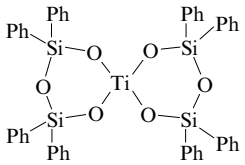
The hydrolysis rate was low. Storage of a sample for 21 days under conditions of chemical equilibrium with the products obtained as a result of formation of titanium–siloxane bonds [Pr^iOH derived from $Ti(OPr^i)_4$] decreased the intensity of a signal in the ^{29}Si NMR spectrum corresponding to the Si–O–Ti bond from 67% to 24%.[123]

The addition of liquid water into the system dramatically increased the hydrolysis rate.[189] In the hydrolysis of spirocyclic titanodiphenylsiloxane **7** ($Ti:H_2O = 1:9$) for 3 days, cleavage of ~50% of Si–O–Ti bonds was observed, whereas the increase in the amount of water in the system to the ratio $Ti:H_2O = 1:44$ led to 90% hydrolysis of the Si–O–Ti bonds in compound **7** as soon as in 1.5 h of treatment.[123] So strong dependence of the hydrolysis rate on the H_2O concentration could point to the cooperative involvement of water molecules in the nucleophilic cleavage of the Si–O–Ti bond to afford a six-centred complex analogous to that observed for rehydroxylation of the strained Si–O–Si bridge [reaction (6)].

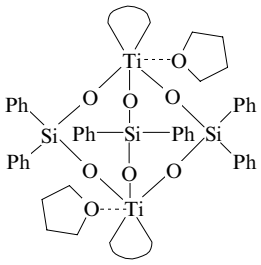
An important factor that affects the hydrolysis rate was the accessibility of the silicon atom to the nucleophilic attack. Studies on the hydrolytic stability of different cyclic titanodiphenylsiloxanes **7**–**11**



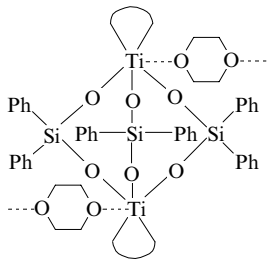
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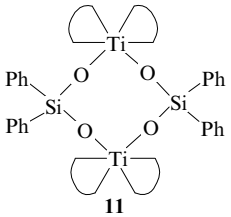
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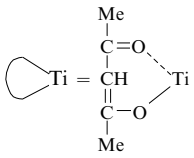
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10



11



has shown that as the Ti–O and Si–O bonds lengths as well as Si–O–Ti bond angles level off, the resistance of compounds against liquid-phase hydrolysis increased (**9**, **10** < **8** < **7** < **11**).[171] The most stable compound **11** virtually failed to react with H_2O in aqueous THF at the $Si–O–Ti:H_2O = 1:1$ ratio for at least 8 h, at 25 °C cleavage of only ~60% of Si–O–Ti bonds occurred in 7 days. Generally, the presence of organic ligands increased the hydrolytic activity of the siloxane bridges (the easily accessible Si–O–Ti bonds underwent complete hydrolysis as soon as in 0.5 h at the ratio $Ti:H_2O = 1:2$).[123]

Studying the properties of 'inversed' systems (titania matrices with deposited silica coatings) also pointed to the substantial effect of structural characteristics of the material on the stability of Si–O–Ti bonds. Thus nine cycles of treatment of the TiO_2 (anatase) surface with trichlorooctadecylsilane in toluene followed by hydrolysis in air for 12 h at room temperature and calcination for 4 h at 550 °C led, according to ^{29}Si NMR data, to the formation of a silica coating the first monolayer of which was bound with titania species by two Si–O–Ti bonds.[121] Anchor bonds of this coating could not be broken even under the action of 30% aqueous H_2O_2 for 24 h.[121] At the same time, the two-step (repeated gas-phase treatment with 1,3,5,7-tetramethylcyclotetrasiloxane under reduced pressure at 80 °C with the photooxidation of the organic ligand[190]) fixation of silica structures on the TiO_2 (anatase) surface made the Si–O–Ti bond resistant against treatment with liquid water for no less than 7 days.

Thus, the formation of a hydrophobic silica layer on the TiO_2 surface, which makes difficult the access of water molecules to silicon atoms involved in the Si—O—Ti anchor bonds, substantially increased the hydrolytic stability of titania–silica materials. In the absence of such protection, SiO_2 was easily washed out by hot (97–100 °C) water in 1–2 h from porous mixed SiO_2–TiO_2 systems prepared by the sol–gel technology.[134, 136]

VIII. Conclusion

The analysis of the presented data makes it possible to conclude that it is the block of the access of water molecules to surface silicon atoms involved in the Si—O—Ti bonds that is among the key factors determining the stability of the titanium–siloxane bonds.

During the liquid-phase hydrolysis in the excess of water, molecules of the latter formed a thin film on the modified matrix surface and easily cleaved the Si—O—Ti bonds to afford individual SiO_2 and TiO_2 phases.

The vapour-phase hydrolysis at low temperatures (T_h < 200 °C), when the SiO_2 surface was saturated with both physically adsorbed water (structure **6**) (removable at 90 °C [191–193]) and water bound to the silicon atoms by the coordination bonds (structures **4**, **5**) [removable in the range of 200–400 °C (Refs 181–183); however, there are indications of its presence up to 650 °C (Ref. 181)] proceeded analogously to the liquid-phase hydrolysis. For the vapour-phase hydrolysis carried out with the simultaneous removal of low-molecular reaction products from the reaction zone at temperatures above 200 °C, when cooperative effects of water molecules on the Si—O—Ti bond were hindered, the structural-chemical characteristics of the support began to play the leading role.

For pyrogenic silica gels with particles of small curvature radii (aerosils), —$TiCl_3$ groups were preferentially present on the surface and access to anchor bonds was free.[14] Hydrolysis of such groups resulted in cleavage of anchor bonds to afford a two-phase system.

It is titanium oxychloride ≡Si—O—$TiCl_3$ groups that are hydrolytically unstable. These groups were formed when the small curvature radius of the silica surface (aerosil particles) or the high degree of dehydroxylation of the surface (as the result of preliminary thermal treatment of the matrix at T > 600 °C) made impossible the formation of additional coordination bonds between this group and the surface due to the large distance between the shielded OH group and the titanium oxychloride structure in the former case or the absence of closely located hydroxy groups in the latter.

For silica gels containing chemisorbed titanium oxychloride groups capable of forming additional coordination bonds with silanol groups remained intact, the resulting surface complex blocked free access of water molecules to the anchor bonds in chemisorbed structures, thus providing the higher hydrolytic stability of the Si—O—Ti bond. The vapour-phase treatment of modified highly-porous silica gels led to the substitution of OH groups for chloride ions involved in titanium-containing fragments. Such a process favoured the chemical assembly of multilayered titania coatings chemically bound with the support surface.

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