Comparative study of structural features and thermal behavior of mixed silica-titania xerogels prepared *via* the peroxo method and the conventional co-precipitation technique

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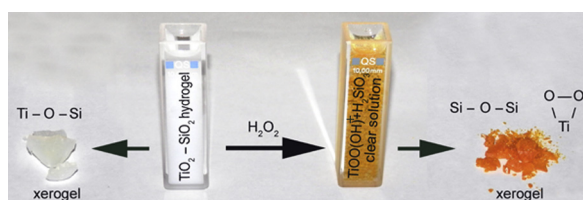[a] *Department of Chemistry, South Ural State University, Lenina Ave. 76, Chelyabinsk, Russia*
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HIGHLIGHTS

- Synthesis of silica–titania xerogels and oxides *via* peroxo-route.
- Homogeneity of the silica–titania samples from FTIR and DR UV investigations.
- Crystallization and phase transformation in the silica–titanias.
- Silica hinders peroxo-group elimination in the composite peroxo-xerogels.
- There are no evidences for existence of Si—O—O—Ti linkages.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Detailed investigation of thermal and structural properties of mixed SiO_2/TiO_2 xerogels prepared *via* the method based on application of a precursor containing peroxo titanic acid and oligomeric silica and by the conventional co-precipitation technique has been presented. Formation of oxide phases from the xerogels prepared *via* the peroxo method and the co-precipitation of inorganic salts has been studied by TG/DSC, FTIR and *in situ* powder XRD techniques. The co-precipitation method provides higher degree of molecular homogeneity of the composite oxide, while in the case of the peroxo route segregation of the oxides takes place. The silica–titania samples prepared by the co-precipitation method include anatase phase, which is stable up to 1000 °C, while TiO_2 in the mixed oxide synthesized by the peroxo method transits to rutile at temperatures near 800 °C. The presented data give no evidence for formation of Si—O—O—Ti peroxo bridges in the xerogels prepared *via* the peroxo method. Peroxo groups in the silica–titania xerogels synthesized *via* the peroxo-method have been found to be more stable in silica–rich samples, compared to pure titania. Thus, these materials hold promise for application as catalysts in oxidation reactions and photocatalysis.

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1. Introduction

Titania and silica–titania are well-known materials with many applications in the fields of photodegradation of organic substances [1–5], acid catalysis [6–8], water splitting [1,3], self-cleaning

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surfaces [1–4], and energy storage devices [9]. These materials attract great interest of researchers in the present time. In spite of a great number of papers on this subject a lot of new studies have been published lately. Recent findings in this field are summarized in the comprehensive reviews [1–3]. Incorporation of titania into silica enhances specific surface area of the composite oxide, decreases titania particle size, provides anatase phase stability and generates acid sites with various strength, all these factors play significant role in the catalytic activity [3]. The strong surface acidity is responsible for the redox active sites and is conducive to suppressing charge carrier recombination. On the basis of theoretical calculations, Seriani et al. [10] suggested that the formation of silica layer onto titania would serve the formation of electron holes on SiO_2/TiO_2 interfaces, which could possibly improve titania photocatalytic activity. In spite of the fact that silica increases the band gap energy of titania in the mixed oxides, there are many papers reporting enhanced photocatalytic activity of silica–titania materials in comparison with pure TiO_2 [3]. The Ti—O—Si linkages are known as the most catalytically active sites of the mixed oxides in organic oxidation reactions [11], thus it is likely that they affect photodegradation process as well.

The differences in hydrolysis rates of silica and titania sources forced researchers to find the ways for their equalization in order to achieve a certain degree of mixed oxide homogeneity [3,12,13]. There are some methods, such as pre-hydrolysis of a silica precursor [14], addition of chelating agents [15–17], using single-source precursor [18,19] are usually applied to ensure the formation of homogeneous silica–titania oxides. Most of the existing methods include the conventional sol–gel technique using toxic alkoxides as precursors, but recently the modern society and industry have taken a turn toward ecologically benign synthetic procedures.

One of the most promising synthetic techniques, alternative to the alkoxide-based one, is the peroxo mediated synthesis. Some reports [20–22] confirm the advantages that the peroxo route has for the synthesis of titanium silicalite and several oxides such as TiO_2, ZrO_2, HfO_2, and others. Application of peroxo complexes for metal oxide synthesis allows tuning the sizes and shapes of the particles and their electrical, optical, catalytic and magnetic properties. It is possible to prepare pure TiO_2 phase (anatase, rutile, brookite) by hydrothermal treatment of oxo-peroxo-glycolato-Ti [23,24] via adjusting the pH values of the media. The peroxo route has been applied for preparation of nanorods, nanotubes, films, discrete, and bulk materials [22]. A simple peroxo mediated technique was applied by Etacheri et al. to synthesize undoped TiO_2, photocatalytically active under UV and visible light, with anatase phase stable up to 900 °C [5]. Also there is great demand for inorganic materials or precursors without any oxidizible ligands, or deleterious trace elements. The presence of stabilizing ligands requires higher annealing temperatures that destroy the initial structure; deleterious elements poison catalysts. A lot of papers were dedicated to preparation of films and bulk materials from peroxo titanic acid (PTA) solution [5,25–36]. The pioneering work, carried out by Ichinose, described the preparation of TiO_2 nanoparticles from PTA [25]. It was also found that the films obtained from PTA sol had excellent adhesion to a substrate. Those results were inferred to be due to the reaction between the substrate and peroxo group [26]. The method was applied for coating silica surface with titania [37], but to the best of our knowledge the formation of the composite bulk oxide from a single-source precursor containing PTA and oligomeric silica, without stabilizing organic additives, has not been reported yet.

Our research presents the insight in the formation of the composite SiO_2/TiO_2 materials from the aqueous precursor containing PTA and oligomeric silica and those prepared by the conventional precipitation route. The peroxo method has been reported earlier [38], but in the present research we avoid using stabilizing ligands, in order to get the understanding of silica–titania interactions. Hereafter we will try to clarify the mechanism of the formation and decomposition of the silica–titania xerogels prepared via different techniques and reveal their structural features, giving special attention to the molecular homogeneity in the silica-titania systems. Also we will establish the role of the preparation in tuning of the local structure of the SiO_2—TiO_2 mixed oxides.

2. Experimental

2.1. Materials

Titanium oxysulfate hydrate ($TiOSO_4 \cdot nH_2O$), containing not more than 17% of H_2SO_4, and hydrogen peroxide H_2O_2 (30 wt.%) were purchased from Aldrich, sodium metasilicate water solution (Na_2SiO_3) was obtained from Cotarcas S.A., and sodium hydroxide (NaOH 98% purity) was purchased from Prolabo. Titanium content in titanium oxysulfate hydrate was determined gravimetrically. Titration method was applied in order to determine silica concentration in Na_2SiO_3 solution.

2.2. Synthesis

Pure titania and the composite silica–titania xerogels, having varied Si/Ti molar ratios, were synthesized similarly to the procedure described elsewhere [38]. Unlike the mentioned method, no organic ligands were used in the present work. The starting solutions were prepared in the following way: the required amount of titanium oxysulfate was dissolved in deionized water and heated at 50 °C in excess of sulfuric acid (added in order to ensure stability toward precipitation of titania); Na_2SiO_3 solution was diluted in order to reach the desired concentrations. The first stage of the synthesis included co-precipitation of sodium metasilicate and titanium oxysulfate solutions and obtaining the silica–titania or pure titania hydrogels in 50 mL of the reaction mixture. For this purpose 25 mL of sodium silicate solution, having varied concentrations equaling 0.00, 0.04, 0.10, 0.20, 0.24, 0.36 M, was dropwise added into 25 mL of titanium oxysulfate solution, having a constant concentration equaling 0.2 M, under vigorous stirring at ambient conditions. The precipitation was induced by addition of 1.5 M solution of sodium hydroxide and then a diluted NaOH solution was used for the adjustment of pH value of the reaction mixture to the value of 4.6. This pH value was chosen because of its closeness to the titanium dioxide isoelectric point in order to minimize the content of adsorbed cations and anions [39]. The hydrogel was centrifuged at 7000 rpm and washed out six times with deionized water. Then the hydrogels were dissolved in 10 mL of 30% H_2O_2 (20-fold excess in relation to Ti^{4+} ions) under vigorous stirring. Dissolution went on for approximately 15 min; it resulted in the formation of a non-opalescent bright orange-colored clear solution, indicating the formation of peroxo titanic acid. Then the decomposition of hydrogen peroxide, accompanied by exothermic effect, took place immediately, which led to bubbling of the evolving oxygen gas, and after approximately 30 min the solubility of the peroxo complex decreased, and the precipitate appeared. The obtained peroxotitanium and silica-peroxotitanium hydrates were left for 24 h, then centrifuged at 7000 rpm and washed out six times with deionized water. Then they were dried in a vacuum box (50 °C, 930 Pa) for 72 h to obtain yellow-colored peroxo xerogels. Pure peroxotitanium xerogels were prepared using the same procedure, but in the absence of silica source. The samples prepared via the peroxo method showed difference in Si/Ti molar ratio in the reaction mixture and in the silica-peroxotitanium xerogels. Among all the synthesized xerogels only several samples were subjected to the detailed characterization. The samples prepared

using the peroxo method with Si/Ti molar ratios equaling 0, and 0.6 were designated as PT and 0.6PTS, respectively. The sample with Si/Ti ratio of 0.6 was chosen for the detailed investigation, as this sample was found to possess the highest silica content after precipitation from H_2O_2-containing solution. The sample prepared *via* the peroxo method having Si/Ti molar ratio of 0.4 (0.4PTS) was also subjected to thermoanalytical characterization. The silica–titania xerogels were synthesized *via* the simple co-precipitation procedure used to prepare SiO_2/TiO_2 hydrogels at abovementioned ratios of matrix-forming elements for comparison reasons; in the same manner they were designated as T and 0.6TS. The co-precipitation procedure included dropwise addition of 25 mL of sodium silicate solution (0.12 M) into 25 mL of titanium oxysulfate solution (0.2 M) under vigorous stirring at ambient conditions. The precipitation was induced by the addition of 1.5 M solution of sodium hydroxide and then a diluted NaOH solution was used for the adjustment of pH value of the reaction mixture to the value of 4.6. The hydrogel was centrifuged at 7000 rpm and washed out six times with deionized water. Pure titania xerogels were prepared using the same procedure, but in the absence of silica source. Further, all xerogels underwent thermal treatment in air at 100, 150, 200, and 250 °C for 7 h.

2.3. Characterization

The hydrogels and the peroxo xerogels, formed by dissolving the silica–titania or pure titania hydrogels in hydrogen peroxide followed by precipitation from a solution, were characterized by elemental analysis (EDS-attachment to scanning electron microscope JEOL JSM 7001F). Thermodiffraction analysis was carried out using X'Pert Philips X-ray diffractometer, operating at Cu Kα radiation. The samples were previously treated at 350 °C for 2 h, in order to remove water and peroxo groups, thus preventing material shrinkage that could affect the measurement results. The heating rate was 5 K min^{-1}, and then the samples were left at the reached temperature for 15 min before acquiring the data. FTIR-spectra were registered using Bruker Tensor 27 spectrometer, with the samples in KBr pellets. Thermoanalytical investigations were carried out in the range from room temperature to 1000 °C by means of simultaneous thermal analyzer Netzsch STA Jupiter 449 F1, equipped with TG/DSC holder, in platinum crucibles at heating rates of 10 and 5 K min^{-1}, with the purge gas (argon) flow rate 40 mL min^{-1}. The curves of thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were registered. The curves of differential thermogravimetry (DTG) were obtained by numerical differentiation of the TG curves. Multipoint BET surface area and micropore volume (t-plot method) measurements were performed in ASAP-2020 apparatus using nitrogen as adsorbate at 77 K. Prior to the adsorption stage the samples were thermally treated to 350 °C for 2 h, in order to remove peroxo groups, then outgassed at 250 °C for 3 h under vacuum.

3. Results and discussion

3.1. Formation of the silica–titania precipitates from H_2O_2-containing solutions

It has been reported earlier, that the interaction between the silica–titania hydrogel and hydrogen peroxide leads to formation of the transparent non-opalescent solution having bright orange or yellow color (depending on pH values) [38]. In the present study, the absence of stabilizing ligands has allowed us to understand the process of precipitation and formation of the amorphous and crystalline oxide phases. The Si/Ti molar ratio equaling 1.8 has been found to be the highest one, which provides obtaining a clear
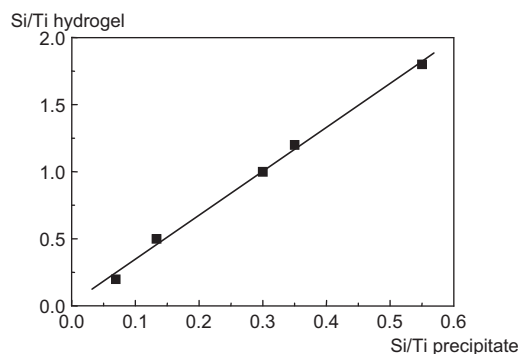

Fig. 1. Dependence between Si/Ti molar ratios in the hydrogels and in the precipitates formed from the H_2O_2 containing solutions.

Table 1
EDS elemental composition of the samples.

Sample	S, (at%)	Ti, (at%)	Si, (at%)	Na, (at%)
T	9.7	90.3	0	0
0.6TS	1.6	60.6	37.8	0
PT	2.4	97.6	0	0
0.4PTS	0	71.7	25.3	3.0
0.6PTS	0	62.3	34.2	3.5

solution after dissolution of the silica–titania hydrogel in hydrogen peroxide. At higher silica content the hydrogel cannot be dissolved completely. The obtained solution loses its stability as hydrogen peroxide decomposes, after 24 h the precipitate is formed. From elemental analysis of the precipitates it has been seen that the Si/Ti ratio in the hydrogels differs from the one in the precipitates after the decomposition of H_2O_2 excess (Fig. 1). With increasing silica content after dissolution and precipitation the greater part of silica has been retained in the solution (confirmed by EDS analysis of the dried filtrate, where amount of titanium left in the solution has been found to be approximately 1–3 at% in relation to Si) or eliminated during the washing step, the other part of it has stayed in the gel-like precipitate.

Elemental analysis of the silica–titania hydrogels and corresponding peroxo xerogels, formed from H_2O_2 containing solutions, reveals that silica is eliminated after isolation of the precipitate from the reaction mixture (Fig. 1). The EDS analysis data for the investigated samples is summarized in Table 1. After the hydrogel is dissolved in the hydrogen peroxide solution, its pH value is in the range 1.2–1.5, indicating the formation of PTA, whose solubility gradually decreases as the excess of H_2O_2 decomposes. The pH values of the mother liquids after the peroxo precipitates are formed have been determined; the results are presented in Fig. 2. The rise of the pH values in the solutions with higher silica content
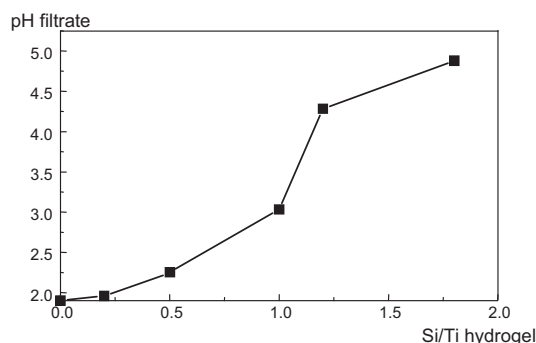

Fig. 2. The values of pH of the reaction mixture after precipitation from the H_2O_2 containing solutions at different Si/Ti ratios in the hydrogels subjected to dissolution.

is more likely to be attributed to more complete decomposition of PTA at these conditions and probably to the formation of the neutral sodium peroxotitania complex. The sodium content in the peroxo xerogels is found to be increasing with the rise of silica content in the hydrogels, it reaches 6 at% in relation to titanium ions when the SiO_2/TiO_2 ratio in the peroxo xerogel is 0.6. Surprisingly, at the pH values higher than 4, rapid polymerization of silica has not been observed. Low concentration of silica and the absence of any electrolyte in sufficient amount to cause rapid coagulation could be the reason for this.

In the previous study [38] we have mentioned that there are two plausible explanations to the dissolution of the hydrogel in H_2O_2. First, Ti^{4+} ions in the hydrogel form soluble peroxo complexes and transit to the liquid phase causing cleavage of Si—O—Ti linkages, which in its turn leads to the formation of oligomeric silica, without tendency to polymerization due to low pH values. Second, the hydrogel can be dispersed in hydrogen peroxide leading to the formation of the non-opalescent solution of the small nanoparticles composed of silica units and titania peroxo species. From the data obtained by EDS analysis the first hypothesis seems to be more reasonable. Since silica is removed after the peroxo precipitate was centrifuged and washed, one can suppose that it stays in the solution in the form of oligomeric silica species. In order to establish the dissolution mechanism, UV–vis spectra and DLS investigations have been carried out. Fig. 3 shows a typical spectrum for a solution, as no significant absorbance is noticed in the visible light range due to light scattering on colloidal particles. Also DLS analysis (the results are not presented) has been unable to detect any particles in the investigated solutions. It is evidenced from ^{29}Si solid state NMR that the incorporation of titanium into silica matrix results in the formation of silica structural units with lower condensation degree compared to those in pure SiO_2 [40]. Thus, it is likely that the interaction of the silica–titania hydrogel with H_2O_2 leads to the formation of water-soluble PTA that, in its turn, causes cleavage of Si—O—Ti linkages and destruction of silica matrix perturbed by the presence of titanium ions, and finally the solution containing PTA and silica in its various oligomeric forms is obtained. The small size of silica species is likely to be below the determination limits of
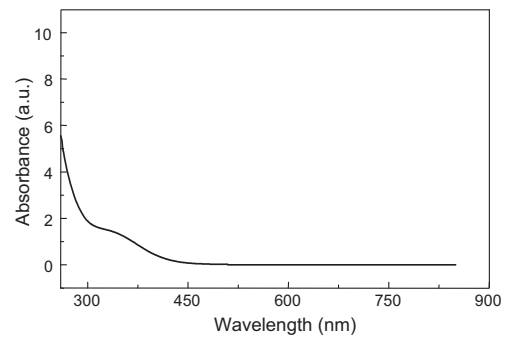

Fig. 3. UV–vis spectra of the solution of PTA and oligomeric silica, prepared by dissolution of the hydrogel in H_2O_2 with Si/Ti molar ratio equaled 1.8.

the techniques used. It is known that silicon does not form peroxo complexes, for this reason, when the concentration of silica in the hydrogel exceeds the value of 1.8, the formation of condensed polymeric Si—O—Si chains starts during the gelation, which is not affected by the presence of H_2O_2. It is reasonable to suggest that titania species start to form the solid phase after the excess of H_2O_2 has been decomposed, and silica is adsorbed on the already formed particles, covering the hydrous peroxotitania colloids.

3.2. Thermal behavior of silica–titania xerogels and peroxo xerogels

The total mass loss according to the thermogravimetry data has been approximately 25% for the titania (T and PT) samples and near 20% for the 0.6TS and 0.6 PTS xerogels, but the DTG profiles reveal that the processes of the decomposition differ significantly for all samples (Fig. 4). The T sample (Fig. 4a) loses its mass in three main stages, in the first stage of decomposition (30–300 °C) physically adsorbed and chemically bonded water is removed, and in the second and third stages (400–800 °C) hydroxyl groups condense to form water, and sulfates evolve. The elemental analysis shows that this sample contains 9.7 at% S in relation to Ti. The co-precipitated
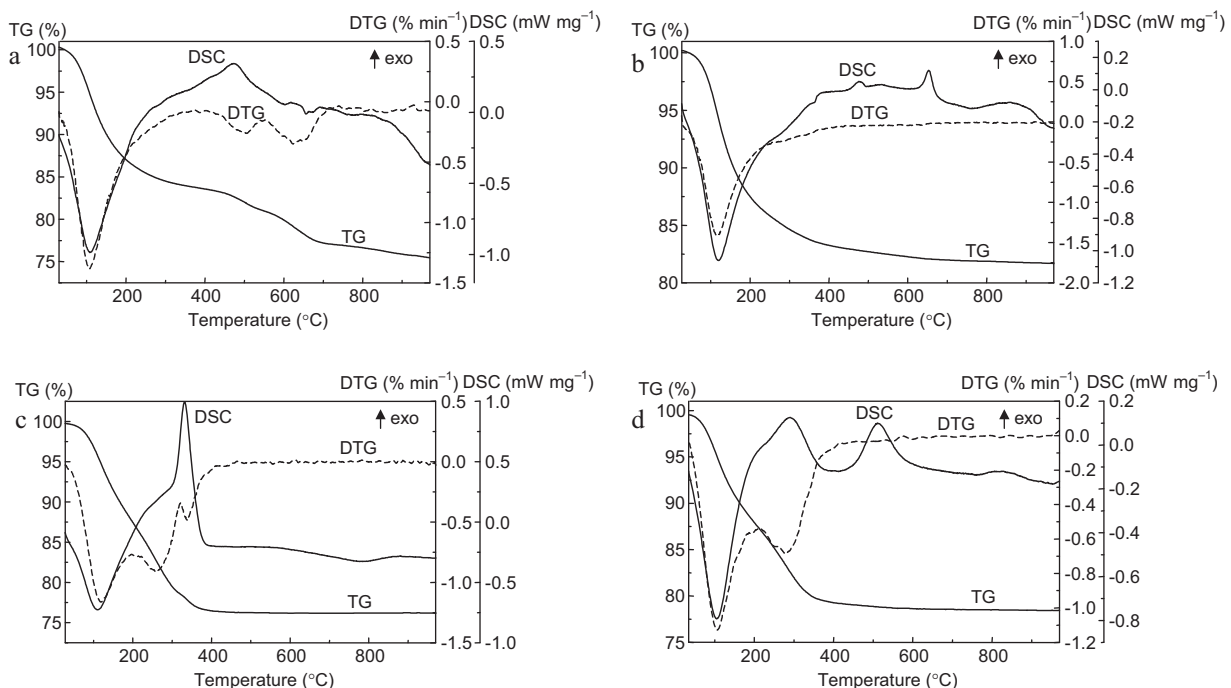

Fig. 4. TG, DTG and DSC curves of the T (a), 0.6TS (b), PT (c) and 0.6PTS (d) samples recorded at the heating rate of 10 K min^{-1}.

0.6TS sample (Fig. 4b) has only one step of the mass loss in the low-temperature region, since the formation of Si—O—Ti bonds have reduced titania basic character, thus resulting in the lower sulfate content in the xerogel. The samples prepared *via* the peroxo method have some new additional features on their thermoanalytical curves. Thermal decomposition of the peroxotitania xerogel (PT) (Fig. 4c) goes in three stages. The first stage is similar to one that the T, 0.6TS and 0.6PTS (Fig. 4a, b and d) samples have, it is also connected to the removal of bonded water of different types. The second stage of mass loss in the temperature range 200–350 °C corresponds to the elimination of peroxo groups from the material, a similar one is observed on the DTG curve of 0.6PTS (Fig. 4d). The same temperature interval, within which peroxo groups are removed, was reported in literature [25,28,30,31,33]. Decreased heating rate in thermoanalytical investigation allows us to separate the effects corresponded to the removal of adsorbed water and peroxo groups elimination, thus enabling us to observe one important event. It is evidenced from Fig. 5 in the samples with high
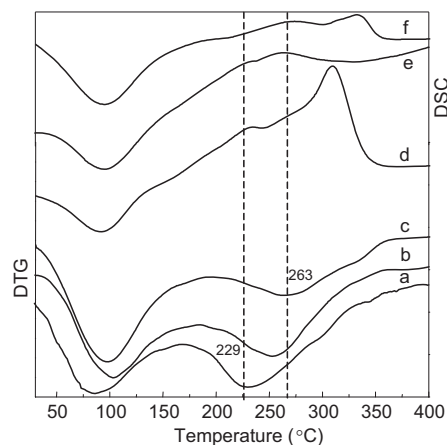

Fig. 5. DTG and DSC profiles of the PT (a and d), 0.4PTS (b and e) and 0.6PTS (c and f) samples recorded at the heating rate of 5 K min⁻¹.
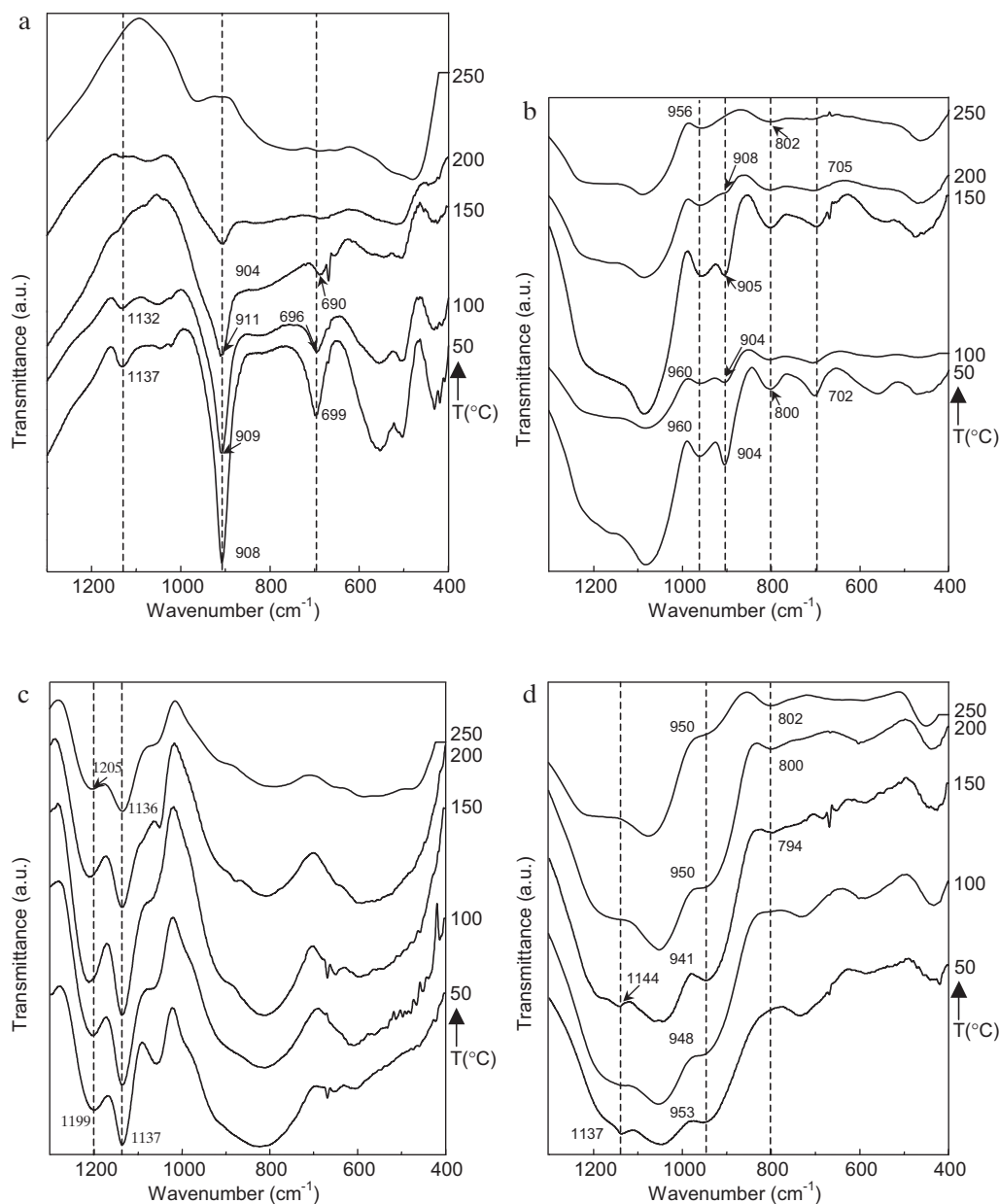

Fig. 6. FTIR spectra of the PT (a), 0.6PTS (b), T (c) and 0.6TS (d) samples thermally treated at different temperatures (temperatures in ordinates).

silica content that elimination of peroxo groups occurs at higher temperatures than in the pure peroxotitania sample. On the DTG curve of the PT sample the peak of peroxo groups decomposition is at 229 °C, while on the DTG curve of the 0.6PTS sample it is at 263 °C (Fig. 5). Delay in elimination of peroxo groups in the samples with high silica content could be explained by the hindered condensation of peroxotitania species encapsulated by or distributed on colloidal silica particles. The FTIR spectra of all xerogels prepared *via* the peroxo method (Fig. 6a and b) clearly show the absorbance at 904–908 cm^{-1}, attributed to O—O stretching vibrations. This peak disappears completely only after heat treatment at 250 °C for 7 h (Fig. 6a and b). The last stage, clearly seen on the DTG curve of PT, is attributed to the removal of hydroxyls, as the result of rapid transformation of titania from amorphous to crystalline state (Fig. 4c). One more important feature on the DSC curves of the investigated samples is the presence of exothermic effects reflecting the phase transition of amorphous titania into crystalline anatase phase. Usually this transition is observed in the range of 350–400 °C [25,28,32], but crystallization can be retarded by dopants or impurities. It is reasonable to deduce from the DSC data that rapid crystallization for the T sample starts near 400 °C, for 0.6TS a number of small-intensity exothermic effects is observed from 350 °C, and the most intense one is seen at 650 °C (Fig. 4a and b). Titania prepared *via* the peroxo method has sharp and intense exothermic effect with the peak at 320 °C and on the DSC curve for the 0.6PTS sample the same process appears at 500 °C (Fig. 4c and d). The reason for the lower crystallization temperature of the PT sample compared to the T one is the absence of substantial amount of sulfates, hindering the condensation of titania species. The 0.6PTS and 0.6TS samples possess no noticeable sulfate content, thus lower temperature of the exothermic effect for 0.6PTS could only be explained by lower degree of molecular homogeneity of the silica–titania.

3.3. Spectroscopic investigation of the silica–titania xerogels

It is known that the stretching mode frequency of the first order O—O bond (a peroxo group) in H_2O_2 is 890 cm^{-1} [41], but it shifts to lower or greater wavenumbers in complexes [42]. The absorption peak at 904–908 cm^{-1}, which is attributed to peroxo groups, has been detected for all samples prepared by the peroxo method (Fig. 6a and b). The shoulder observed at 690 cm^{-1} is assigned to vibration of Ti—O—O bonds. In the FTIR spectra of both as-prepared and thermally treated samples T, TS, 0.6PT, and 0.6PTS the peaks located at 430 and 500 cm^{-1} are likely due to vibration of Ti—O bonds in TiO_2 lattice (Fig. 6a–d). The absorption at 960 cm^{-1} can be assigned to the contribution from vibrations of Si—O—Ti linkages and silanol groups, but the intensity of the vibration of Si—OH groups is usually low, that is why the peak in this region is considered as the characteristic of Ti—O—Si bonds [40] (Fig. 6b and d). The vibration at 800 cm^{-1}, corresponding to symmetric stretching of Si—O—Si bonds [43] appears on the spectrum of 0.6TS, only when it is treated at high temperatures (Fig. 6d); in case of the 0.6PTS sample we can detect it even in the as-prepared xerogel (Fig. 6b). Apparently, this fact confirms that a part of silica is polymerized and segregated from the mixed oxide. In Fig. 6a, c and d, we can observe the presence of the peaks at 1137 cm^{-1} for the T, PT, 0.6TS samples and at 1199–1212 cm^{-1} only for T, which corresponds to vibration of sulfate groups [44]. From the EDS analysis, that has been described earlier, only the T sample shows significant presence of sulfur. We can observe that the PT and 0.6TS samples also have some amount of sulfates, but in very small quantities (also according to EDS analysis), that after 150–250 °C they are overlapped with other peaks and become not detectable (Fig. 6a and d). There is no absorption in the range of wavenumbers of the O—O or Ti—O—O vibrations in the samples prepared without hydrogen peroxide addition. The peak located at 904 cm^{-1} on the spectra of the peroxo
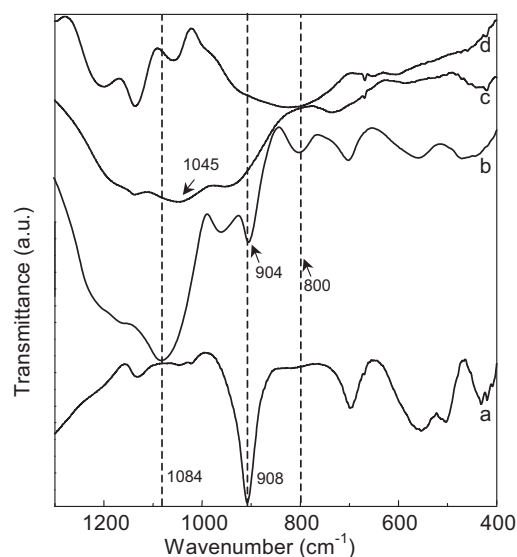

Fig. 7. FTIR spectra of the as-prepared samples that were prepared *via* the peroxo method (a – PT, b – 0.6PTS) and co-precipitation (c – 0.6TS, d – T).

xerogel disappears only after heating at 250 °C for 7 h (Fig. 6a and b), something similar was observed in literature [25,28,30,31,33] and was expected on the basis of the thermoanalytical curves. FTIR spectroscopy is known to be a simple and powerful method to detect the formation of oxo-bridged linkages between silicon and some transition metals [45,46]. The band near 1100 cm^{-1} is assigned to asymmetric stretching vibrations of Si—O—Si bonds in silica; it has tendency to shift toward lower wavenumbers, when some silicon atoms in SiO_2 matrix are substituted by other metal cations [40]. On the spectrum of the 0.6TS sample (Fig. 7) this band is shifted to 1045 cm^{-1}, while the displacement of this peak on the spectrum of the 0.6PTS xerogel is not so obvious. Moreover, symmetric vibrations of Si—O—Si units of smaller intensity indicated by the band at 800 cm^{-1} also confirm that silica is in the segregated state in the sample prepared *via* the peroxo method. Thus, one can conclude that the co-precipitation method provides higher degree of molecular homogeneity of the composite oxide.

There is a discussion about the existence of Si—O—O—Ti bonds in titanium silicalites. On the basis of DFT study Munakata et al. suggested the formation of Si—O—O—Ti moieties during the catalytic epoxidation of olefins [47]. However, it has not been confirmed by
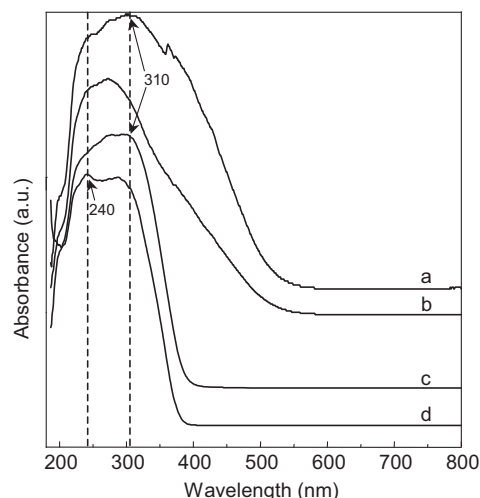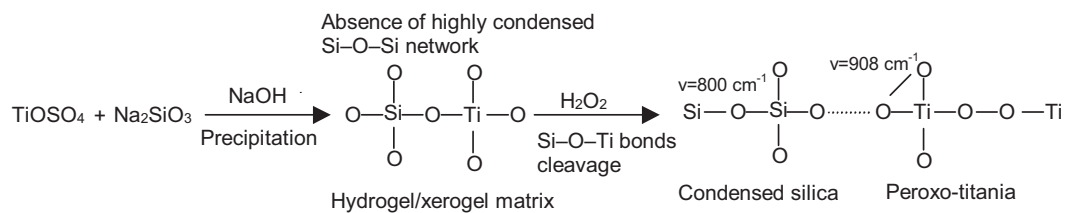

Fig. 8. DR UV spectra of the PT (a), 0.6PTS (b), T (c), 0.6TS (d) as-synthesized samples.

Scheme 1. . Schematic representation for the formation of the silica–titania xerogels *via* the co-precipitation and peroxo methods.
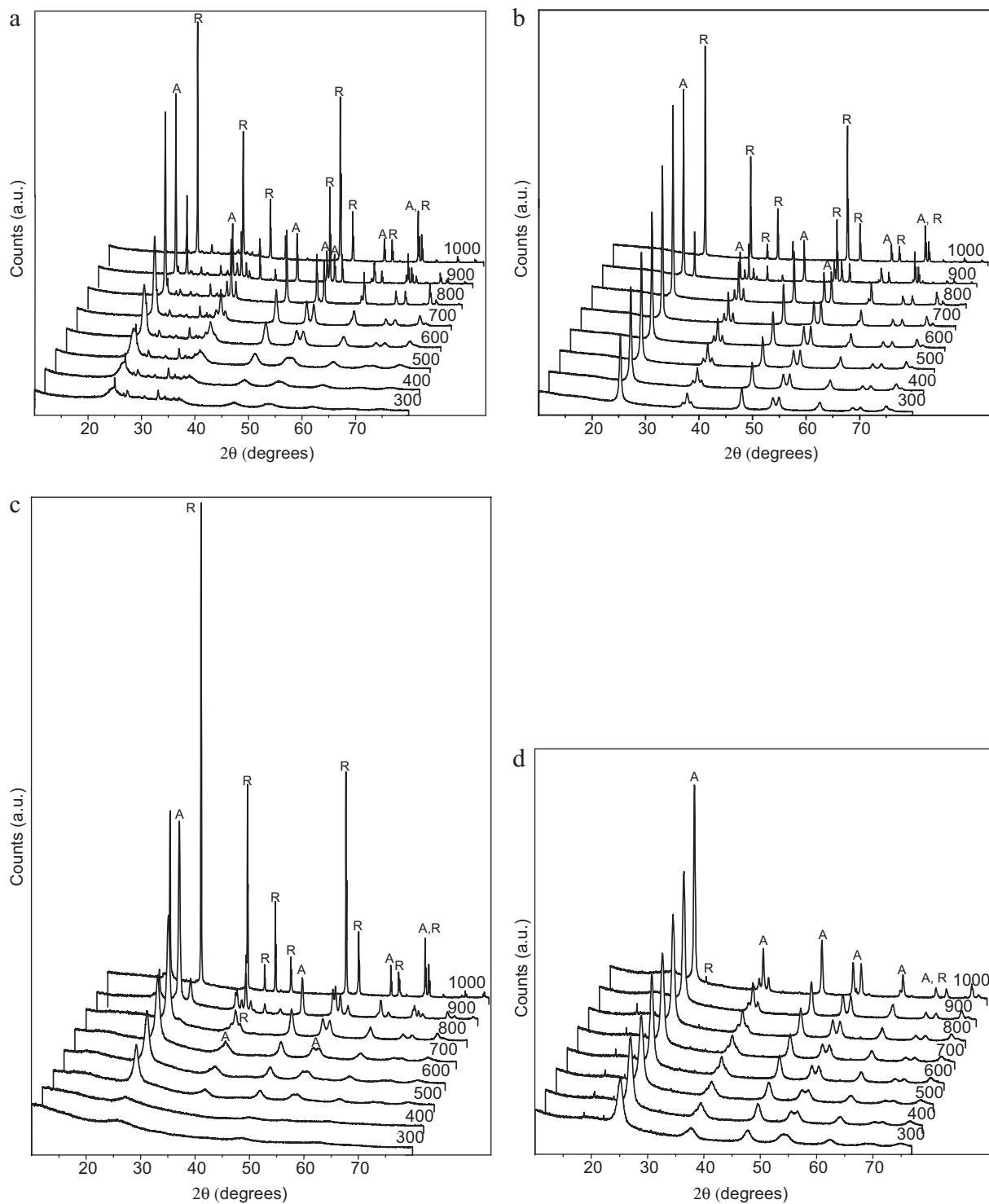

Fig. 9. XRD patterns of the T (a), PT (b), 0.6PTS (c), and 0.6TS (d) samples registered at different temperatures.

experimental investigations [48]. Analyzing the data obtained in the present research, we also find no direct evidence for Si—O—O—Ti existence. From the results of FTIR experiments it is seen that no new bands appear on the spectrum of the PTS sample, which cannot be found on PT or TS spectra, and no shifting of O—O or Ti—O—O vibrations is observed as well. Also, it is likely that the condensation of Si—O—O—Ti bonds would have led to Si—O—Ti oxo-bridges and not to formation of separated silica and titania species, but the samples prepared *via* the peroxo method have been found to be in the more segregated state than the precipitated ones.

DR UV spectroscopy gives deeper insight in some structural features of amorphous titania-based materials, it is considered indispensable for the determination of the coordination state of titania species [49]. The samples prepared *via* the peroxo method absorb light in the visible range of wavelengths (Fig. 8a and b) due to formation of the colored peroxotitania species. The peroxotitanate (PT) and pure precipitated titania (T) have the peaks of absorption at 310 nm (Fig. 8a and c), indicating the presence of big TiO_2 clusters in anatase phase, where titanium has coordination number of 6. The increasing silica content causes the peaks to appear on the spectra at about 240 nm, it implies that Si—O—Ti bonds are formed and the coordination number of titanium decreases from 6 to 4, also the sizes of titanium dioxide crystals dispersed in silica are reduced, which could be detectable on the UV spectrum due to quantum size effect. The bands at 240–250 nm are due to the charge transfer process in isolated tetrahedral $[TiO_4]$ or $[HOTiO_3]$ units [49]. It is worth noticing that the band at 240 nm is more prominent on the spectrum of 0.6TS (Fig. 8d), implying the higher degree of titanium incorporation into the silica matrix compared to the sample prepared *via* the peroxo method. The schematic representation of the formation of the silica–titania xerogels *via* both methods is depicted in Scheme 1.

3.4. XRD and BET analyses

The sample of pure TiO_2 prepared by the simple co-precipitation starts to crystallize into anatase phase after temperature exceeds 500 °C (Fig. 9a), which is in good agreement with the results of thermal analysis. Anatase phase remains stable at temperatures as high as 800 °C, and with further heating it fully transits to rutile at 1000 °C. Titania formed *via* the peroxo method even at 300 °C [25] is in the form of well-crystallized anatase (Fig. 9b), its crystallinity gradually improves at higher temperatures, and only after 900 °C the presence of rutile is detected. This sample, similarly to the T one, shows high thermal stability of the anatase-to-rutile phase transition, but the reasons for this are different. It is likely that anatase in the T sample is stabilized by the presence of anionic impurities, causing the formation of the defected structure; after sulfate groups are removed, the transformation of the metastable crystalline phase into the stable one takes place. The stabilization of anatase phase by anionic impurities was also observed by other researchers [50,51]. In the titania sample prepared *via* the peroxo route no significant amount of sulfates is present to be the reason for stabilization. Etacheri et al. while studying similar system came to the conclusion that the high stability of anatase phase up to 900 °C could be caused by the oxygen vacancies formed in the result of peroxo group decomposition [5]. Thermodiffractional analysis confirms the supposition, made on the basis of TG/DSC and FTIR investigations, about the temperature ranges of peroxo groups decomposition and the thermal effects that are assigned to this event. The first exothermic effect in the range of 250–350 °C, observed on DSC curves of the peroxo xerogels could only correspond to elimination of peroxo group, and not to phase transition. According to thermodiffractional analysis the 0.6PTS sample stays amorphous up to 400 °C (Fig. 9c), which is higher than the temperature of the first exothermic effect. Unexpectedly, the presence

of silica in the sample has not influenced the temperature of the anatase-to-rutile phase transformation. Titania in this mixed oxide starts to form rutile phase at temperatures similar to the pure titania samples. At the same time the 0.6TS sample, prepared *via* co-precipitation, has not shown any presence of rutile phase at temperatures up to 1000 °C (Fig. 9d). Anatase phase stability in this sample cannot be explained by sulfate groups presence, because of their trace quantities in the sample, it is more likely to be attributed to incorporation of silica into TiO_2 cell. Increase of the anatase-to-rutile transformation temperature by silica addition was also observed by other researchers [51]. From the FTIR and DR UV investigations the higher degree of molecular homogeneity of the co-precipitated sample is obvious. The incorporation of titania into silica matrix causes retardation of the phase transformation due to hindering of the diffusion process and formation of defects in the anatase crystals. Unexpectedly, the silica–titania prepared *via* the peroxo method and having lower degree of molecular homogeneity shows retardation of the crystalline phase formation from the amorphous state. It is possible that the peroxo method favors higher dispersion of the small titania peroxo species among SiO_2, as similar fact was observed in the case of molybdenum peroxocomplex supported on zirconia [52]. Thus higher temperatures are necessary to induce their condensation and crystallization, as a consequence.

The samples prepared *via* both methods are microporous and have low surface areas, these values for 0.6TS and 0.6PTS are equal to 37 m^2/g and 68 m^2/g, respectively. The co-precipitation method allows obtaining the silica–titania material with high degree of molecular homogeneity that does not favor formation of the developed surface [46]. The segregation in the mixed oxide prepared *via* the peroxo method somehow improves SiO_2/TiO_2 textural characteristics, besides, it causes an increase in micropore volume from 0.012 cm^3/g for the 0.6TS sample to 0.016 cm^3/g for the 0.6PTS one.

4. Conclusion

Interaction of the silica–titania hydrogel with H_2O_2 leads to formation of the solution containing peroxo titanic acid and silica oligomeric species. The titania and silica–titania xerogels prepared *via* the proposed technique contain stable peroxo groups, which, according to thermal and IR analyses, are totally removed only after treatment at 250 °C for 7 h. Thus these materials are promising catalysts for peroxo oxidation and epoxidation reactions. It has been established that the co-precipitation method provides higher degree of homogeneity of the material, in terms of formation of Si—O—Ti bonds, compared with the peroxo method. This is the reason for the lower temperature of the anatase-to-rutile phase transition in the composite silica–titania sample synthesized *via* the peroxo route than in the silica–titania sample prepared *via* the conventional precipitation of inorganic salts, where anatase phase is stable up to 1000 °C. Thus, it is likely that titania species have stronger affinity to peroxo groups than to silica, and silica is only adsorbed on the surface of the amorphous peroxotitania particles formed in the process of precipitation from the solution of peroxo titanic acid and oligomeric silica. Combining the results of FTIR, TG/DSC and XRD investigations we have established that the presence of peroxo groups inhibits the formation of crystalline phases from amorphous TiO_2 in the silica matrix. Moreover, the decomposition of peroxo groups occurs at higher temperatures in the silica containing samples. We have not found any evidence for formation of Si—O—O—Ti peroxo-bridges in the xerogels prepared *via* the peroxo method.

Acknowledgements

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