



## Properties and segregation stability of the composite silica-zirconia xerogels prepared via “acidic” and “basic” precipitation routes

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### ABSTRACT

Two series of the composite silica-zirconia xerogels with various  $\text{SiO}_2/\text{ZrO}_2$  molar ratios have been prepared by the “acidic” and “basic” precipitation methods. It has been established that the ways of synthesis have significant effect on surface area, morphological and thermal properties of the xerogels. In addition, the segregation processes in dependence on post-synthetic treatment have been examined in the gels with various molar compositions. Optimal molar composition for each synthetic route in terms of the phase segregation stability of the composite  $\text{SiO}_2\text{-ZrO}_2$  xerogels has been proposed.

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### 1. Introduction

Silica gels have many unique properties. However they also have many disadvantages limiting their application as catalysts and adsorbents, as well as precursors for ceramic manufacturing. Therefore, the interest for composite materials synthesis appeared. These composites are produced by the isomorphous substitution of a part of silicon atoms in the oxide matrix for transition metal ions, in particular zirconium. Such composites have found their applications in production of ceramics of high hardness and strength [1], anti-corrosive coatings [2], and photonic materials [3,4]. Many researchers reported that the insertion of zirconium atoms in the silicate matrix favors increasing of thermal stability of tetragonal phase of zirconium dioxide [5–10], promoting catalytic [11–15] and sorption activity of the composite materials in comparison with the individual oxides or xerogels [16]. The main reason of appearing of new unique physicochemical properties in the systems of the composite oxides is the formation of Si–O–Zr bonds on the surface, as well as in the bulk of the material. The formation of these bonds in the composite  $\text{SiO}_2\text{-ZrO}_2$  gels was studied by the computational methods [17], their existence was confirmed by means of NMR  $^{17}\text{O}$ , NMR  $^{29}\text{Si}$  and EXAFS [18,19]. F. del Monte et al. [6] proved that the formation of the Si–O–Zr linkages took place during the wet synthesis, but not in the next stage of thermal treatment.

Availability of the Si–O–Zr heterolinkages, their stability and homogeneous distribution in the volume and on the surface of the composite oxide, determines much of the material's properties. Mixed  $\text{ZrO}_2\text{-SiO}_2$  oxides contain strong acid sites, whereas individual oxides of silica and zirconia have only weak acid sites, as it has been shown in the study [20]. Obviously, one of the main factors, determining the formation of the Si–O–Zr linkages, is the molar  $\text{SiO}_2/\text{ZrO}_2$  ratio in the precursor solutions. C. Flego et al. [21] observed the densification of Lewis acid sites and decreasing of the number of strong Brønsted acid sites with rising of zirconium content in the composite  $\text{ZrO}_2\text{-SiO}_2$  oxide. That is why tracking the segregation process of the composite xerogel in dependence on the molar ratio of matrix-forming components, post-synthetic treatment and the synthetic method is so important. Infrared spectroscopy and thermal analysis are the methods successfully applied for this purpose [9,13,19,22–28].

In spite of the good deal of the information, accumulated for the last decades of investigations of the composite xerogels, as well as silicon and zirconium oxides, the processes of their formation and the effect of the initial synthetic conditions on the properties of these materials are still unclear. Many researchers used alkoxides as the precursors and chelating agents for lowering hydrolysis rate for the synthesis of  $\text{SiO}_2\text{-ZrO}_2$  gels [4,6,10]. However, alkoxides are expensive and toxic. Second, the necessity of the organic part removal from the gel after the synthesis requires high temperature treatment that can cause condensation and elimination of functional hydroxogroups from the surface of the xerogel. In turn, it results in the decreasing of sorption and catalytic activity of the material. The control of hydrolysis rate is even more complicated in case of using inorganic salts as the precursors. Obviously, low concentration of

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the reagents and adjustment of the synthesis conditions make possible the preparation of the homogenous composite materials with varied physicochemical and structural properties.

Several investigations [8,16,23,28,29] were devoted to the synthesis and study of the characteristics of the composite  $\text{SiO}_2\text{-ZrO}_2$  oxides and xerogels prepared from inorganic precursors without chelating and structure-directing agents. At the same time in those studies no attention was paid to the influence of the sequencing of the precursor addition into the reactor during the synthesis stage of the composite gels or precipitates. It is known that hydrated zirconia can be prepared via “acidic” and “basic” routes, which differ by the sequencing of precursors addition into the reactor [30–32]. It has been found that these two synthetic ways have drastic effect on textural and thermal properties of the synthesized samples. Our previous studies also have indicated the similar effect of synthetic procedure on the sorption, thermal and morphological characteristics of the composite  $\text{SiO}_2\text{-ZrO}_2$  xerogels, prepared at equimolar  $\text{SiO}_2/\text{ZrO}_2$  ratio [33–36].

The present investigation reports the effect of the molar  $\text{SiO}_2/\text{ZrO}_2$  ratio in “acidic” and “basic” synthetic routes on surface area, thermal and morphological properties and on the segregation stability of the composite silica-zirconia xerogels. Xerogels have been prepared from inorganic salts of silicon and zirconium in absence of chelating and structure-directing agents.

## 2. Experimental

### 2.1. Materials and methods

The composite gels have been synthesized according to the procedure described elsewhere [33–36], by the two synthetic methods of co-precipitation. “Basic” route has been accomplished by the addition of the zirconium oxychloride solution into the sodium metasilicate solution (SZ), whereas reverse order of the reagent addition has been applied in “acidic” method (ZS). Initial concentrations of the sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ) and zirconium oxychloride ( $\text{ZrOCl}_2$ ) solutions are 0.1 mol/L. Molar ratio of  $\text{SiO}_2$  to  $\text{ZrO}_2$  in the gels equals 1, 2, 3 and 4 (hereafter designated as  $S_{50}Z_{50}$ ,  $Z_{50}S_{50}$ ,  $S_{67}Z_{33}$ ,  $Z_{33}S_{67}$ ,  $S_{75}Z_{25}$ ,  $Z_{25}S_{75}$ ,  $S_{80}Z_{20}$ ,  $Z_{20}S_{80}$  respectively). The ratio has been set by the decreasing zirconium oxychloride concentration at the constant sodium metasilicate content. The final pH values of the synthesis have been chosen on the basis of the previous studies [33–35], they equal 9 for the “basic” method and 10 for the “acidic” one. The pH value of the mother liquor has been adjusted by the 0.2 mol/L NaOH and HCl solutions after addition of the silicon and zirconium salts. Individual silica and zirconia xerogels have been prepared by the acidic and basic hydrolysis of  $\text{Na}_2\text{SiO}_3$  and  $\text{ZrOCl}_2$  salts (hereafter designated as S and Z respectively). Syntheses have been carried out at room temperature ( $20 \pm 2$  °C). Concentration of zirconium oxychloride solution has been measured gravimetrically. Concentration of sodium metasilicate solution has been determined using titration by the standard solution of hydrochloric acid in the presence of methyl orange indicator. In order to control reproducibility, no less than four samples have been prepared for each synthesis condition. The gel-like precipitates have been aged in the mother liquor for 1 day, then they have been filtered and washed thoroughly with distilled water until the negative reaction on the initial ions. The prepared hydrogels have been kept in air at room temperature for a while, then, after drying in the vacuum box (30 °C, 930 Pa) during 3 weeks, stored in dessicator at room temperature over anhydrous calcium chloride. Further, xerogels have undergone thermal treatment in air at 50, 100, 150, 200 °C for 72 h in the thermostat. All reagents used in the current study have been of analytical grade.

### 2.2. Characterization

Infrared spectra have been registered in the range 1800–400  $\text{cm}^{-1}$  using Bruker Tensor 27 spectrometer. Samples have been pressed in potassium bromide (KBr) pellet under dynamic vacuum, in order to reduce the amount of air and physically adsorbed water, with sample/KBr mass ratio equaling 1/100. For each specter no less than 120 scans with a resolution of 2  $\text{cm}^{-1}$  have been recorded and averaged.

Thermoanalytical investigations have been carried out in the range from room temperature to 1000 °C by means of the simultaneous thermal analyzer Netzsch STA Jupiter 449C in corundum crucibles, using corundum sample holder with the thermocouple of S-type at the heating rate of 10 K/min, with the purge-gas (dry air) flow rate of 40 mL/min. The curves of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) have been registered. The curves of differential thermogravimetry (DTG) have been obtained by computational differentiation of the TGA curves.

SEM-images have been obtained with the help of the scanning electron microscope Jeol JSM7001F. Samples have been platinum-coated with 2–3 nm magnetron sputtered layer prior to the analysis.

The specific surface area of the samples has been calculated by BET method from the results obtained from low temperature nitrogen adsorption using Sorbi-MS analyzer. No less than three measurements have been carried out for each sample and the systematic error for this type of measurement was found to be not higher than 5%.

## 3. Results and discussion

### 3.1. Thermal analysis

The thermal analysis of SZ composite gels, dried under vacuum at 30 °C temperature, has revealed the decreasing of total bonded water amount and the DTG peak shifting in the direction of low-temperature range with decreasing of zirconium content in gels (Fig. 1a). It is logical to suggest that water, contained in the equimolar composite, is bonded more tightly compared to water of the samples with higher silica content. The shoulder is seen on the DTG curves obtained for the samples with a  $\text{SiO}_2/\text{ZrO}_2$  ratio of 3 and 4, thus indicating possible separation of silica phase.

From the XRD analysis of equimolar silica-zirconia xerogels [36] it is known that the exothermic effect on DTA curves of investigated samples reflects crystallization process of amorphous zirconia, contained in the composite, into its tetragonal phase (Fig. 1b). The DTA curves have shown that: the higher the silica content, the more the crystallization is hindered and the more the exothermic effect is shifted to the high temperature region. The greatest difference of the exo-effect temperatures has been found to be 30 °C.

Similar to SZ xerogels, the highest content of bonded water is also observed for the equimolar  $Z_{50}S_{50}$  sample compared to xerogels with higher  $\text{SiO}_2/\text{ZrO}_2$  molar ratio (Fig. 1c). However, its thermoanalytical curve profile is much more complicated than for other ZS and SZ samples. The DTA curve of the  $Z_{50}S_{50}$  sample has two well-defined endothermic effects and the doubled exo-effect. The TGA curve has a step near 400 °C with 3.25% mass loss. This step corresponds to the partial crystallization of amorphous zirconia, as it has been shown in [36]. The step is gradually disappearing as zirconia content is decreasing; it is almost absent on the TGA curve of  $Z_{33}S_{67}$ , and weight loss there equals only 0.6%. The abovementioned features of thermal decomposition of the composite  $Z_{50}S_{50}$  xerogels give grounds for the presupposition that at equimolar  $\text{SiO}_2/\text{ZrO}_2$  composition the partial segregation of the composite takes place, which implies separation of zirconium oxyhydroxide rich phase and its crystallization at temperatures common to individual hydrous zirconia. Strangely, the crystallization process in  $Z_{50}S_{50}$  is not accompanied by a sharp exothermic effect, usual for some transition metal oxides such as:  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{TiO}_2$ ,  $\text{CrO}_3$ , etc., and known as “glow phenomenon”. Srinivasan and Davis studied this

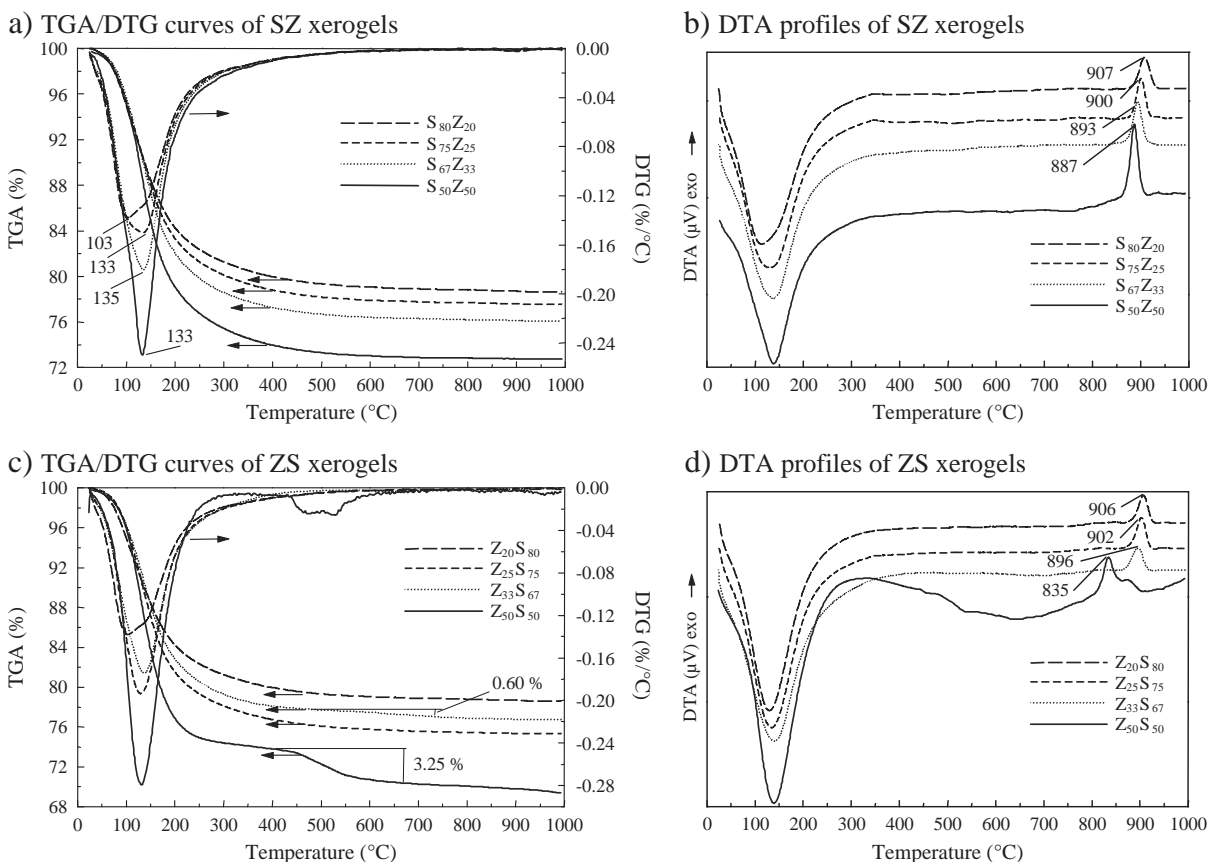


Fig. 1. Thermoanalytical curves of the composite silica-zirconia xerogels.

phenomenon in systems of individual zirconia, hafnia and their composites [37]. They have discovered that in the mixed oxide crystallization event appears before an exothermal peak is detected. Detailed investigation, applying thermal analysis, X-ray diffractometry, surface area measurement and microscopy, has convincingly proved that crystallization and “glow phenomenon” are two different events, and the last one is the reflection of the coalescence of preformed single crystallites into larger crystalline domains. Thus, one can suppose that the coarsening of initially formed crystallites is hindered in the  $\text{SiO}_2\text{-ZrO}_2$  oxide system due to high degree of distribution of individual zirconia species in the composite oxide that is the reason for the absence of the exothermal effect after the phase transition. The endothermic effect and the mass loss, in turn, are connected with the release of bridged hydroxyls as the result of the crystallization process. For ZS samples with higher silica content and for all SZ xerogels the shifting of zirconia crystallization to higher temperatures for all SZ xerogels has been observed; it can be related, in accordance with the authors of [38,39], to homogeneous mixing of two hydrous oxides in the composite.

### 3.2. FTIR study

IR spectroscopy allows obtaining some important information about the structure of the composite silica-zirconia materials. Particularly, it helps in detection of Si–O–Zr linkages, whose presence informs us about the existence of the composite homogeneous areas in mixed oxide systems. Moreover, Si–O–Si linkages can also reveal themselves on the IR-spectra, thus the tracking of the individual silica separation from the composites is made possible.

Individual silica has the broad band in IR region centered at  $1100\text{ cm}^{-1}$  due to asymmetric Si–O–Si stretching vibration of  $\text{TO}_3$  mode and the  $\text{LO}_3$  part of asymmetric stretching giving the shoulder at  $1200\text{ cm}^{-1}$  [40], as well as the band at  $980\text{ cm}^{-1}$  attributed to

Si–OH bonds stretching vibrations [22]. The peak centered at  $980\text{ cm}^{-1}$  can also appear on IR-spectra as the result of partial substitution of silicon atoms in the silica matrix by transition metals, therefore, it also should be assigned to Si–O–Zr bonds vibration [23]. Since the peak in this IR region is very broad and can be assigned to vibration of various bonds, it is unsuitable for tracking of silica phase in the composite xerogels. However, it gives some information about incorporation of transition metals into the silica matrix.

It is also hard to assign the peak near  $480\text{ cm}^{-1}$  to definite bond vibrations, it is usually assigned to Si–O–Si bridges, but it also corresponds to  $\text{ZrO}_8$  fragments of tetragonal zirconia [6]. Despite the amorphous nature of samples, they possess some similarity to crystalline structures, as has been concluded on the basis of Raman spectra of zirconium hydroxides [41]. Thus, this range of wavenumbers is also unreliable in the sense of individual silica separation tracking. There are many studies devoted to individual and composite oxides of silicon and zirconium [5,6,22,23,42] reporting that  $\text{TO}_2$  mode symmetric stretching of Si–O<sup>−</sup> ring structure appears on the spectra near  $800\text{ cm}^{-1}$ . No other vibrations are assigned to this range, so it has been chosen as the most reliable range of wavenumbers for the tracking of silica separation from the composite xerogel.

IR spectra of all samples dried at  $30\text{ }^\circ\text{C}$  (Figs. 2 and 3) have peaks in the range of wavenumbers from  $975$  to  $1060\text{ cm}^{-1}$ , which correspond to Si–O–Zr bonds vibration [6,22,24]. No absorbance, characterizing Si–O<sup>−</sup> ring structure vibration, is observed near  $800\text{ cm}^{-1}$  for  $\text{S}_{50}\text{Z}_{50}$ ,  $\text{Z}_{50}\text{S}_{50}$ ,  $\text{S}_{67}\text{Z}_{33}$ ,  $\text{Z}_{33}\text{S}_{67}$  samples (Figs. 2a, b and 3a, b). Further decreasing of zirconium content in precursors for composite gel synthesis leads to the formation of xerogels, whose IR spectra show bands assigned to Si–O<sup>−</sup> bond vibrations. Thus, individual silica phase formation is observed only for  $\text{S}_{75}\text{Z}_{25}$ ,  $\text{Z}_{25}\text{S}_{75}$ ,  $\text{S}_{80}\text{Z}_{20}$ ,  $\text{Z}_{20}\text{S}_{80}$  samples.

At the same time, separation of hydrous zirconia phase from the composite is observed for the  $\text{Z}_{50}\text{S}_{50}$  sample, as it has been suggested

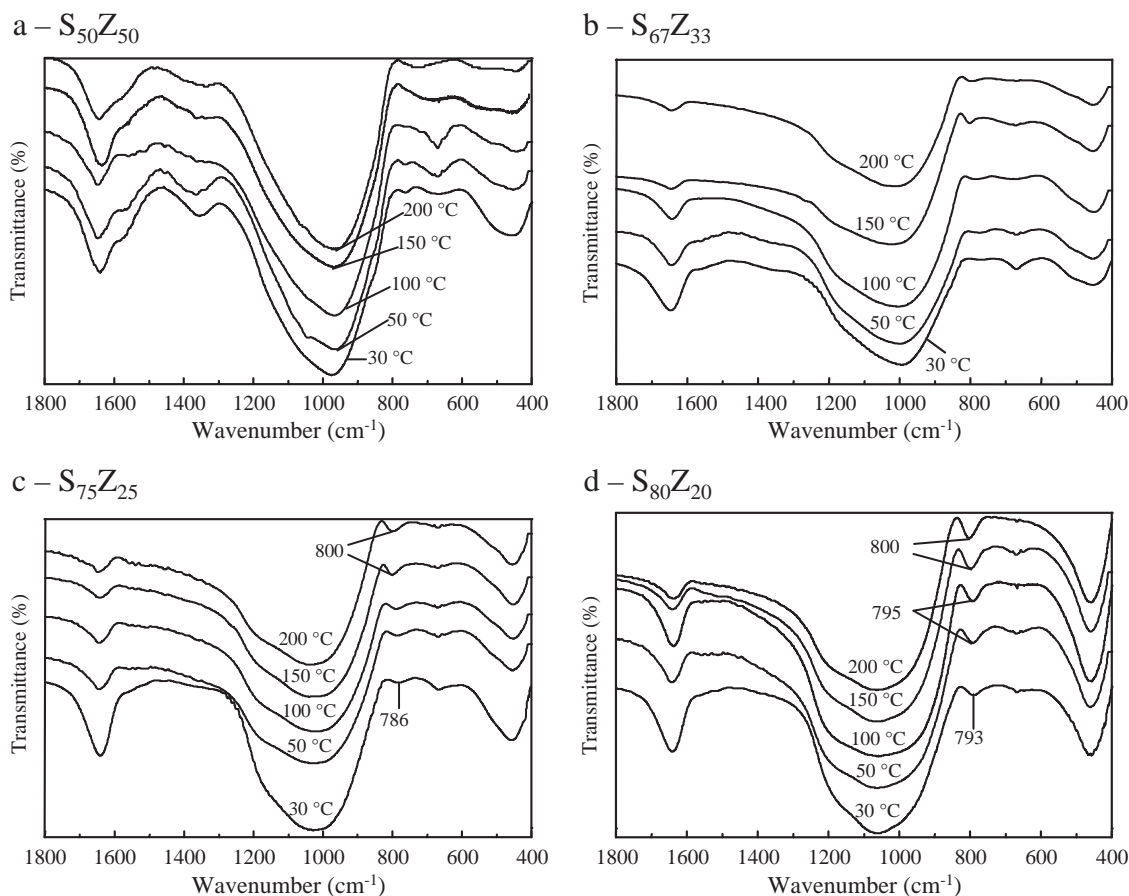


Fig. 2. IR spectra of SZ xerogels thermally treated at various temperatures.

earlier on the basis of thermal analysis. In agreement with the results of thermal analysis, IR spectrum of this sample definitely shows absorbance at 1580, 1400 and 1350  $\text{cm}^{-1}$  (Fig. 3a), which are observed only for individual hydrous zirconia [36,41]. According to the data presented in the study [41], the abovementioned bands correspond to bidentate carbonate, formed as a result of atmospheric  $\text{CO}_2$  adsorption on unsaturated  $\text{O}^{2+}\text{-Zr}^{4+}$  pairs. Similarly,  $\text{S}_{50}\text{Z}_{50}$  sample has low-intensity absorbance at 1350  $\text{cm}^{-1}$ , indicating the presence of oxo- or hydroxogroups belonging to zirconium, but no other methods, such as TGA/DTA and XRD [36] analyses have been able to detect zirconia separation.

From the samples prepared via “basic” route,  $\text{S}_{50}\text{Z}_{50}$  xerogel is found to be the most stable to thermally induced segregation. No indication of silica phase separation is observed even after thermal treatment at 200 °C during 72 h (Fig. 2a). The peaks near 800  $\text{cm}^{-1}$ , characterizing Si–O $^-$  bonds, are observed for SZ xerogels with lower zirconium content after thermal treatment at 100 °C (Fig. 2b). The intensity of such peaks is rising with increasing of treatment temperature.

Composite phase of the xerogels synthesized via “acidic” method are more stable under thermal treatment. Thermal treatment of  $\text{Z}_{50}\text{S}_{50}$  (Fig. 3a) and  $\text{Z}_{33}\text{S}_{67}$  (Fig. 3b) samples at all applied temperatures hasn’t led to appearance of characteristic vibrations of Si–O $^-$  on IR spectra. Such bands are observed only for  $\text{Z}_{25}\text{S}_{75}$  and  $\text{Z}_{20}\text{S}_{80}$  xerogels. There is a band observed on IR spectra of  $\text{Z}_{25}\text{S}_{75}$  and  $\text{Z}_{20}\text{S}_{80}$  samples (Fig. 3c) at 780  $\text{cm}^{-1}$ , which for  $\text{Z}_{25}\text{S}_{75}$  shows no changes of position with the increasing of thermal treatment temperatures, while for  $\text{Z}_{20}\text{S}_{80}$  it is gradually shifting towards higher wavenumbers: at 100 °C its value equals 786  $\text{cm}^{-1}$ , 795  $\text{cm}^{-1}$  at 150 °C, and 800  $\text{cm}^{-1}$  at 200 °C.

### 3.3. Surface area and morphology

During the study it has been found that surface area of the composite silica-zirconia xerogels is highly affected by the  $\text{SiO}_2/\text{ZrO}_2$  molar ratios and synthetic methods (Fig. 4). The samples prepared at equimolar  $\text{SiO}_2/\text{ZrO}_2$  ratio via “basic” method have values of surface area twice smaller than individual xerogels of silica and zirconia. Decreasing of zirconium content in the composite xerogels leads to the formation of samples with more developed surface, whose values reach those found for individual silica and zirconia gels. It is worth noticing that the highest value of surface area (375  $\text{m}^2/\text{g}$ ) among all samples has been observed for  $\text{S}_{80}\text{Z}_{20}$  xerogel. The effect of small amount of zirconium in the composite gel (8–10 at.% Zr), resulting in the increasing of its surface area, was observed earlier [5,23,43]. However, we haven’t found any explanation of this phenomenon in the analyzed literature.

Similar dependence of surface area increasing with decreasing zirconium content in the composites has also been observed for xerogels prepared via “acidic” route.  $\text{Z}_{50}\text{S}_{50}$  and  $\text{Z}_{33}\text{S}_{67}$  samples have a surface area less than 5  $\text{m}^2/\text{g}$ , which is smaller to that for individual xerogels in two orders of magnitude (Fig. 4). SEM observations are in good agreement with surface area measurement. SEM images clearly show difference in porous structure of SZ and ZS gels with various Zr loadings (Fig. 5).

Miller [38], in his turn, supposed that decreasing of surface area is connected with a rise of homogeneity in the mixed silica-zirconia oxides, so low surface area can be an indirect evidence of high degree of homogeneity of investigated materials. Thus, one can conclude that  $\text{SiO}_2/\text{ZrO}_2$  molar ratio equaling 2 favors the formation of the most homogenous composite, prepared via “acidic” route, as only minor phase



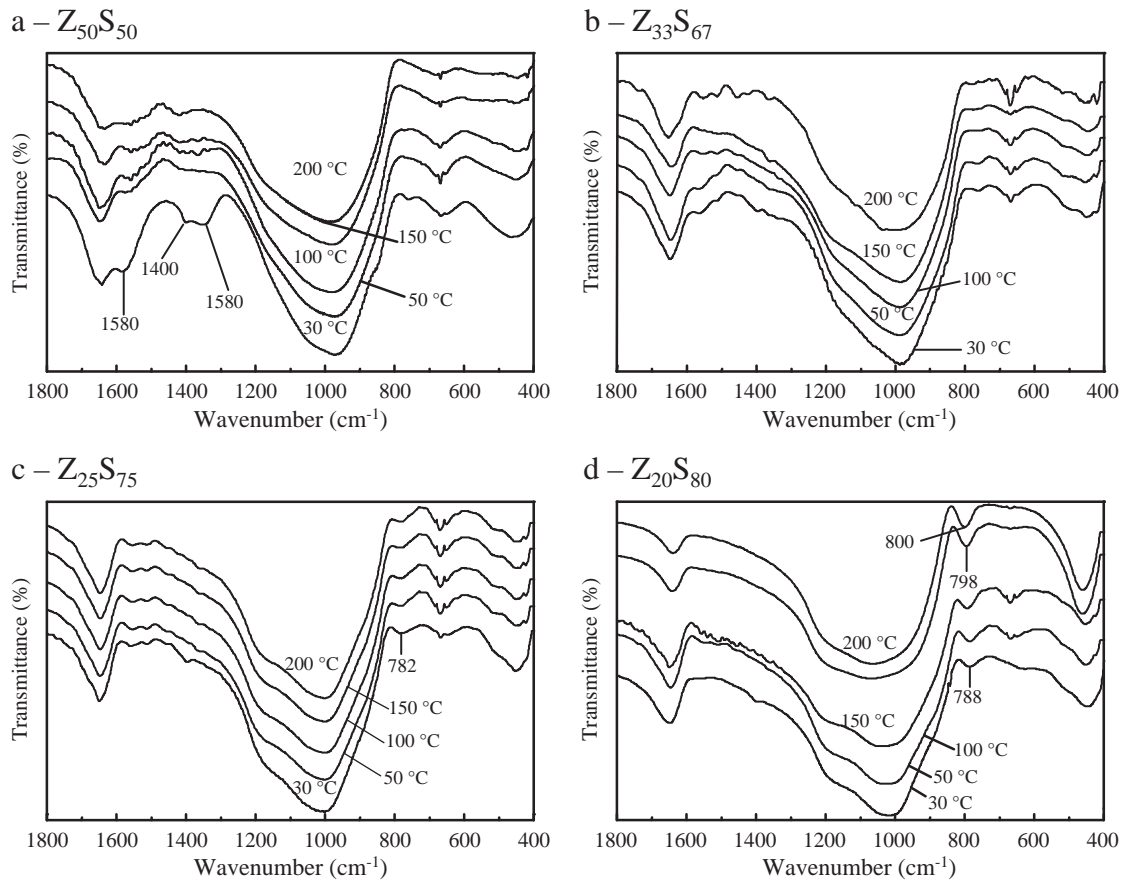


Fig. 3. IR spectra of ZS xerogels thermally treated at various temperatures.

separation of zirconia from the composite is observed by the thermal analysis. The difference in coordination numbers of silicon and zirconium, usually 4 and 8 correspondingly [38,44] could be one of the satisfactory explanations of this fact. In addition, the passing of the reaction mixture during the synthesis stage through the isoelectric points of individual oxides [45,46] and processes of polymerization, dissolution and particle growth, thoroughly discussed by Iler for silica as dependent on pH values of the medium [46], play important roles in segregation behavior of the composite oxide. One can suppose that high solubility of silica species and their low polymerization rate in alkali medium promotes the interaction with hydrated zirconia species and formation of homogeneous silica-zirconia composite via the “basic” route even at their equimolar ratio. The system does not pass through any isoelectric points, so no particle recharging appears providing the interaction

mechanism of two matrix-forming elements is unchanged during the whole preparation stage. During the other precipitation route the system passes through isoelectric points of both oxides that can, probably, lead to the formation of zirconia domains unreacted with silica. It should be mentioned, that SEM and TEM techniques have been unable to detect directly the xerogel segregation due to their high degree of homogeneity.

Explanation of the formation of equimolar SZ and ZS xerogels and the differences in their properties was presented in detail earlier [36].

#### 4. Conclusion

It has been shown that synthetic method (“acidic” or “basic”) and  $\text{SiO}_2/\text{ZrO}_2$  molar ratios determine structural, morphological and textural properties of the composite silica-zirconia xerogels. The “acidic” route, implying the addition of sodium metasilicate solution into the reaction mixture containing zirconium oxychloride, favors formation of the gels with higher stability of the composite xerogel to segregate at high temperatures and lower values of specific surface area. The sample with  $\text{SiO}_2/\text{ZrO}_2$  molar ratio of 2 ( $\text{Z}_{33}\text{S}_{67}$ ) has the highest stability to segregate among the others. The “basic” synthetic route, implying the addition of zirconium oxychloride solution into the reaction mixture containing sodium metasilicate, favors the formation of the xerogels with developed surface area, at  $\text{SiO}_2/\text{ZrO}_2$  molar ratio of 4 ( $\text{S}_{80}\text{Z}_{20}$ ) higher values are reached when compared to those observed for individual silica and zirconia xerogels. The samples at equimolar  $\text{SiO}_2/\text{ZrO}_2$  ratio, prepared via “basic” route, have shown no segregation detectable by the applied investigation methods. One can conclude, that variation of the  $\text{SiO}_2/\text{ZrO}_2$  ratio in the precursors and methods of precipitation, even in absence of chelating or structure-directing agents,

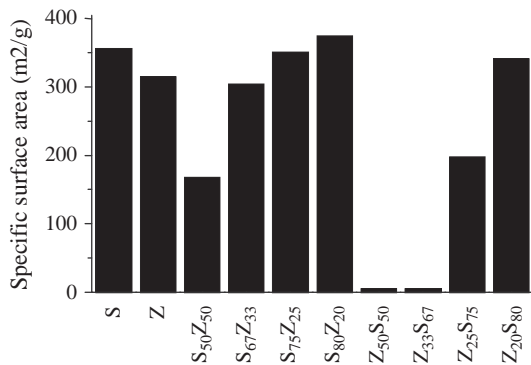


Fig. 4. Specific surface area of the individual and composite silica-zirconia xerogels.

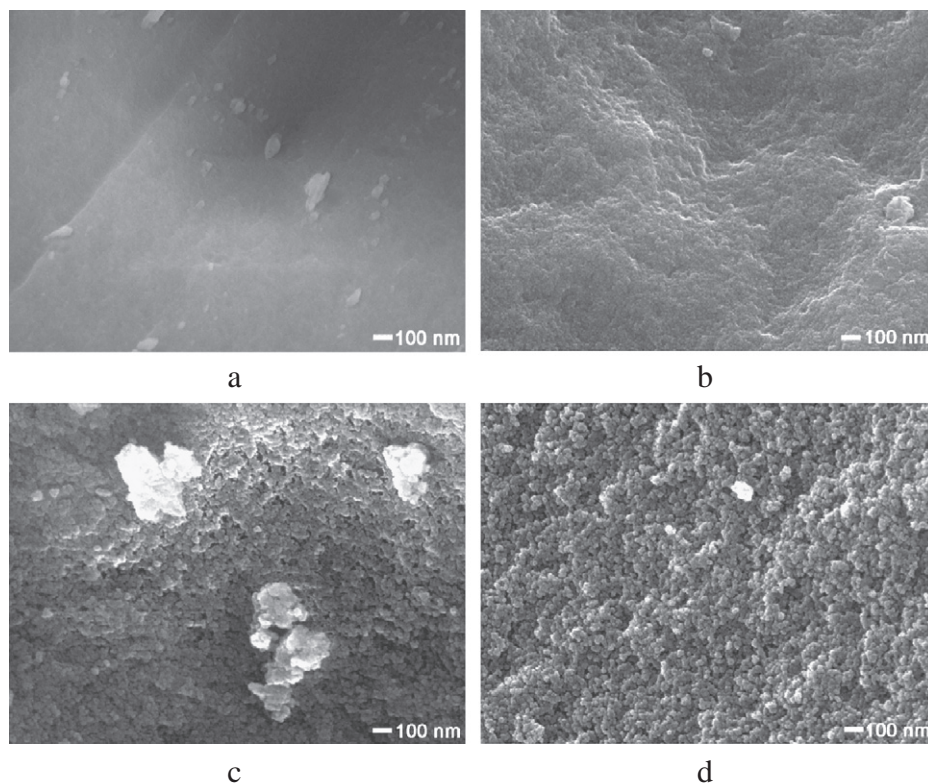


Fig. 5. SEM images of the ZS and SZ samples. a)  $Z_{33}S_{67}$ , b)  $Z_{20}S_{80}$ , c)  $S_{50}Z_{50}$ , d)  $S_{80}Z_{20}$ .

allows us to successfully control textural, morphological, thermal and structural properties of the composite silica-zirconia xerogels.

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