

Thermal behavior of the composite xerogels of zirconium oxyhydroxide and silicic acid

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Abstract Gels were prepared via sol–gel method by addition of zirconium oxychloride solution into sodium metasilicate (SZ) and sodium metasilicate solution into zirconium oxychloride (ZS) at varying final pH. Si/Zr molar ratio equaled 1/1. Synthesized gels were dried with calcium chloride until they reached a constant mass. SEM and nitrogen adsorption analysis have shown that SZ gels have surface area 175–200 m² g⁻¹, consist of 20–30 nm grains. ZS samples have surface area about 1 m² g⁻¹, consist of grains smaller than 10 nm. Thermal and X-ray phase analysis have shown that transition of amorphous ZrO₂ to crystalline form shifts from 430 to 850–870 °C for SZ gels. Unlike zirconia gels phase transitions that proceed in order: “amorphous (430 °C)—tetragonal (800 °C)—monoclinic (1,000 °C) phases”, the monoclinic phase in ZS gels appears immediately after transition from amorphous to crystalline state; the tetragonal phase in SZ samples is stable until 1,000 °C.

Keywords Ceramics · Oxide materials · Sol–gel processes · Thermal analysis · X-ray diffraction · Phase transitions

Introduction

The hydrous oxide and oxyhydroxide systems are especially interesting because of the wide range of their applications such as: precursors for ceramic manufacture [1], catalyst supports [2], and adsorbents [3]. At the same time the problems of thermal stability increasing and certain crystalline modifications stabilizing are very important for this kind of compounds. Preparation of composite oxides of silicon, zirconium, and aluminum, as it was demonstrated in papers [4–6], favors formation of compounds with higher phase transition temperatures than those for individual oxides.

In the sol–gel technology of composite oxide systems the special measures preventing segregation are needed, this is especially important when the precursors have significantly different reactivity [7]. The problem of segregation can be solved by prehydrolyzing the less reactive precursor [8], by using the complexing agents slowing down hydrolysis in the synthesis process [9], or by the introduction of the less reactive precursor into a solution of the more reactive one [7]. In the current paper special attention is paid to the influence of reagent introduction order during the synthesis of the composite gel of zirconium oxyhydroxide and poly-silicic acid upon features of phase transitions of prepared samples under thermal treatment.

Experimental

Synthesis

The composite xerogels have been obtained as adsorbents for extraction of metal cations from water solutions. Solutions of sodium silicate and zirconium oxychloride

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have been used as the precursors for making individual and composite gels via the sol–gel method. Final concentrations of gel-forming compounds in the mixture (when all components have been mixed) equal 0.05 mol L^{-1} . This concentration value has been chosen because it is the minimal concentration, which makes possible the gel formation of polysilicic acid during 24 h at room temperature. In papers [10, 11] it has been shown that slowing the hydrolysis rate allows to obtain more ordered structures containing more accessible sorption centers than in the materials prepared by the fast hydrolysis method. Obviously, one of the ways of slowing down hydrolysis rate is to decrease the concentrations of the precursors. Sodium silicate solution has been hydrolyzed by hydrochloric acid (0.2 mol L^{-1}) until the pH value reaches 7.0 to obtain the gel of polysilicic acid (designated as S). Individual gels of zirconium oxyhydroxide (designated as Z) have been prepared by addition of ammonia (0.2 mol L^{-1}) into oxychloride solution until final pH 10.0. Two methods of composite gels preparation have been used: (1) the addition of zirconium oxychloride solution into the mother liquid-containing solution of sodium silicate (these samples are designated as SZ); (2) the addition of sodium silicate solution into zirconium oxychloride (these samples are designated as ZS). Silicon:zirconium mole ratio in the mother liquids of composite gels is 1:1. Prepared gels have been conditioned for 24 h in a thermostat at $20 \text{ }^\circ\text{C}$, desalted, filtered, and dried with calcium chloride at room temperature until the constant weight is achieved. All used chemicals are of analytical grade. Synthesis conditions have been chosen on the basis of data obtained elsewhere [12]. Samples prepared at those conditions, among the others, have the highest sorptive capacity measured in static conditions by the simple batch method in relation to Ca^{2+} and Y^{3+} ions.

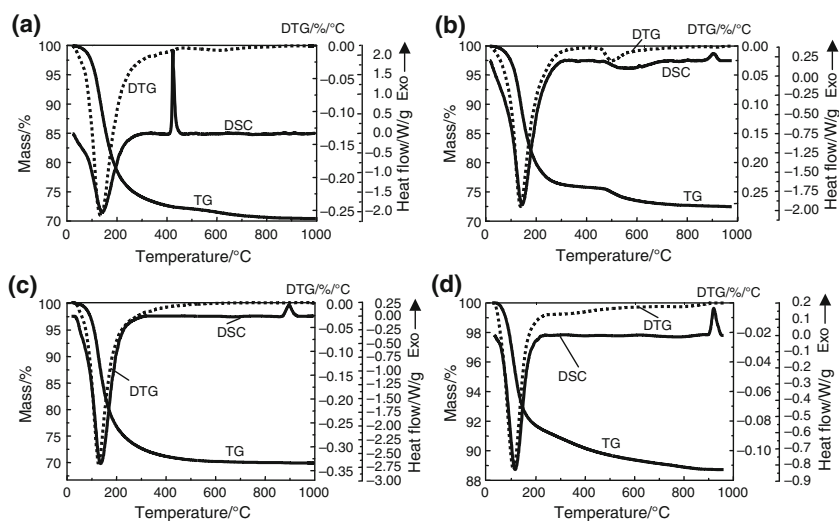
Characterization

Netsch 449C DSC/TGA analyzer has been used for combined differential scanning calorimetry and thermogravimetry analysis of the samples. Thermal analysis has been carried out in an air flow at the heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, in the temperature range from room temperature to $950 \text{ }^\circ\text{C}$. Powder X-ray diffraction patterns have been registered from the samples annealed at certain temperatures, which were chosen according to the results of thermal analysis, using Dron-3M ($\text{CuK}\alpha$) diffractometer. The samples have been annealed at the same conditions and at the same heating rate as they were for thermal analysis experiments. The scanning electron microscope Jeol JSM-7001F has been used to obtain microphotographs. Samples have been platinum covered before obtaining SEM images. FTIR investigation of samples has been carried out with the use of Bruker Vertex 80 FTIR spectrometer at $4,000\text{--}400 \text{ cm}^{-1}$ from samples powdered together with KBr and pressed into pellets. The method of nitrogen adsorption at 77 K on the Sorbi-MS analyzer has been used to calculate the specific surface area by the BET equation. Before measuring specific surface area the xerogels have been degassed at $200 \text{ }^\circ\text{C}$ in the nitrogen flow.

Results and discussion

Simultaneous thermogravimetry and differential scanning calorimetry is the useful technique in the study of inorganic adsorbents and ion-exchangers based on different types of oxide and phosphate materials, as it was shown in the papers [13, 14]. Under heat treatment the individual gels of polysilicic acid and zirconium oxyhydroxide undergo dehydration, dehydroxylation, and crystallization processes. After crystallization amorphous silica transits to

Fig. 1 Thermoanalytical curves of individual and composite gels: **a** Z, **b** ZS, **c** SZ, **d** S



crystalobalite [15], zirconium oxide initially forms the metastable tetragonal phase (T-phase), then the stable monoclinic phase (M-phase) [16]. On the DSC curves crystallization usually appears as exothermic effect. Exothermic effect observed on thermoanalytical curves of Z gels at 430 °C (Fig. 1a) is shifted to the temperature range 850–870 °C in the composite gels (Fig. 1b, c). Similar exothermic effect shifting was observed in investigations of other two-component oxide systems, containing zirconium dioxide [5, 6, 8]. Exothermic effect temperature increasing can be explained by the steric hindrances, occurring because of the high degree of disorder in this type of a gel [5]. The effect at 920 °C (Fig. 1d) corresponds to the crystallization of amorphous silica.

On thermoanalytical curves of ZS samples (Fig. 1b) the TG curve has a step at 480 °C, a similar step is also present on TG curve of Z gels (Fig. 1a), but its value is less than the same for ZS. Mass loss at that temperature range is attributed by some authors [17, 18] to bridged hydroxyl groups removal during the intense polycondensation process resulting in dioxide crystallization. Data obtained by the means of X-ray diffractonal analysis (Fig. 2) show formation of T-phase in Z and ZS samples, but the presence of M-phase of zirconium dioxide is also observed in the composite. Above-mentioned dehydroxylation process in Z sample starts after crystallization of zirconium dioxide to T-phase whereas in ZS samples these processes start simultaneously. Thereby, supposedly, this step on the TG curves at this temperature range is attributed to transition of tetragonal to monoclinic zirconia. The DSC curve of ZS

thermal decomposition shows no exothermic effect indicative of amorphous zirconia crystallization. With further thermal treatment up to 1,000 °C ZrO_2 in Z samples almost completely transits to monoclinic phase (Fig. 2a), whereas in ZS samples T- and M-phases ratio stays unchanged, and only the degree of crystallinity rises (Fig. 2b).

Thermally induced phase transitions in SZ samples differ from those in other gels. Thermal analysis curve profile of the SZ gels resembles the profiles of similar curves for S gels (Fig. 1d). Significant difference is in the amount of removed water, which is almost three times higher in SZ gels than in S gels. Almost all the water is removed until 300 °C, i.e., until the crystallization

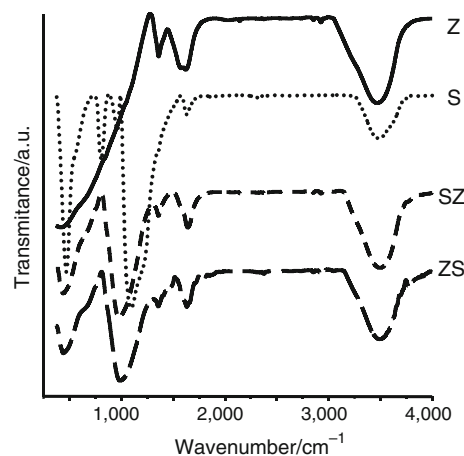


Fig. 3 IR spectra of individual and composite gels

Fig. 2 X-ray diffraction patterns of individual and composite gels, annealed at various temperatures: **a** Z, **b** ZS, **c** SZ, **d** S, T tetragonal phase, M monoclinic phase, C cristobalite

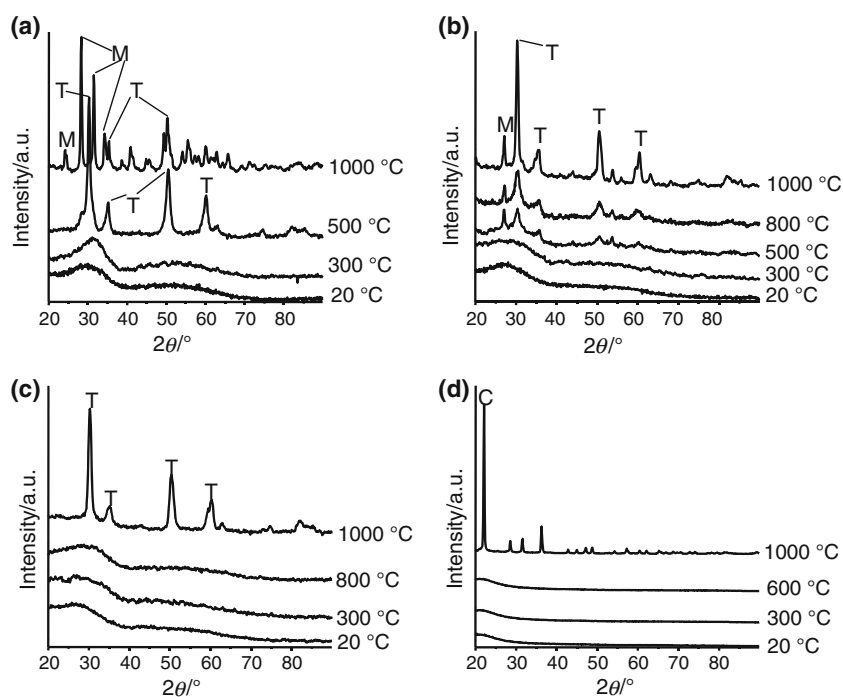
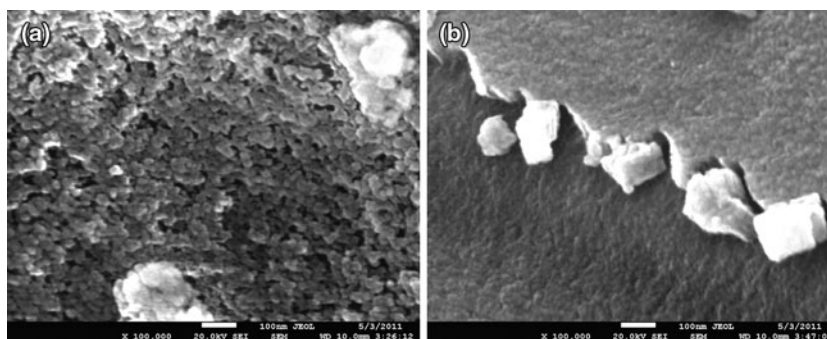


Fig. 4 SEM photographs of SZ (a) and ZS (b) samples



processes take place. According to powder X-ray diffraction analysis SZ gels are in amorphous state up to 800 °C. T-phase formation of zirconia occurs at 850–870 °C, which is accompanied by the exothermic effect on the DSC curve (Fig. 1c). T-phase of zirconium dioxide in SZ gels is stable up to 1,000 °C (Fig. 2c).

S samples have no phase transitions up to 920 °C and then almost completely transit to cristobalite (Fig. 2d). This process is accompanied by the significant exothermic effect on the DSC curve (Fig. 1d). X-ray diffractational and thermal analyses show no indication of cristobalite phase presence in the composite gels. Probably in these samples the crystallization of amorphous silica is shifted to higher temperatures.

Differences of properties of ZS and SZ samples, investigated in the present paper, are consequences of different rates of formation and particle growth of zirconium oxyhydroxide and silicic acid. In the initial stage of SZ synthesis the drops of the zirconium oxychloride solution fall into the mother liquid, containing sodium silicate, and having pH value higher than 12. These conditions favor the intensive hydrolysis of zirconyl ions, as a consequence the grains of zirconium oxyhydroxide are formed. Further addition of the zirconium oxychloride solution gradually decreases pH value of the mother liquid because of low pH value of the added reagent. At the same time, the rate of zirconium oxyhydroxide nucleation slows down, but the rate of formed particles growth increases. Due to the high solubility of silica at pH values above 9 [19], the growth of composite gel particles continues by deposition of dissolved silicic acid on initially formed larger particles of zirconium oxyhydroxide. Because of the high rate of the solid phase of zirconium oxyhydroxide formation on the initial stage of synthesis, the particles stay small and separate, then they react with silicic acid.

In the process of ZS preparation the drops of sodium silicate fall into the mother liquid, with pH value below 2. Iler established that at pH values below 2 the rate of polymerization and nucleation of polysilicic acid was low. Therefore, negatively charged SiO_3^{2-} ions can react with positively charged zirconium tetramers, co-condense and form highly polymeric structures.

The explanation of composite gel formation offered above finds confirmation in quantum-chemical computations [20] as well as in the experimental data. In the papers [21–23] it was found by the means of IR spectroscopy that bonds Si–O–Zr were present in mixed polysilicic acid and hydrous zirconia systems prepared via sol–gel method. IR spectra of composite gels (Fig. 3) show bands at 987–984 and 668–662 cm^{-1} , which are attributed to stretching and deformation vibrations of Si–O–Zr bonds [21–23]. These bands appear on spectra of ZS gels as well as SZ gels.

SEM shows differences in morphology of the SZ and ZS gels. SZ samples have highly porous structure are composed of grains 20–30 nm in diameter, ZS gels consist of grains less than 10 nm (Fig. 4). It should be mentioned; the grains of ZS samples are linked with each other and are packed more compactly than grains of SZ gels. That can be the reason why ZS gels have specific surface area that is less by two orders of magnitude in comparison with other samples. Values of surface area of investigated gels are: S—356, Z—168, SZ—167, ZS—1 $\text{m}^2 \text{g}^{-1}$.

Conclusions

In composite gels prepared with a different order of reagent introduction, the reactivity of which is significantly different, no segregation has been observed. Thermal stability and specific surface area of composite gels of zirconium oxyhydroxide and polysilicic acid depend on the order of reagent introduction during the synthesis stage.

Introduction of zirconium oxychloride into sodium silicate favors formation of the gel with grain sizes about 20–30 nm and specific surface area 167 $\text{m}^2 \text{g}^{-1}$. During heat treatment zirconium dioxide contained in these gels transits to tetragonal crystalline phase that is stable up to 1,000 °C.

Sodium silicate solution introduction into the mother liquid-containing zirconium oxychloride leads to formation of gels having specific surface area about 1 $\text{m}^2 \text{g}^{-1}$ and consisting of highly polymeric densely packed grains about 10 nm in diameter. Zirconium dioxide containing in that

gels starts to crystallize at 480 °C and forms the monoclinic phase along with the tetragonal one. With further heat treatment the crystallinity of samples instantly increases at 850 °C but the phase ratio stays almost unchanged up to 1,000 °C.

Order of reagent introduction into the mother liquid at the synthesis stage allows to successfully control the structure formation of composite gels of zirconium oxyhydroxide and polysilicic acid and also to insure formation and stabilization of tetragonal zirconia.

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