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THERMAL ANALYSIS OF BINARY SYSTEM Al_2O_3–SnO_2 OBTAINED BY SOL-GEL TECHNIQUE
Part I. Oxidative atmosphere

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A series of Al_2O_3–SnO_2 catalysts with Al_2O_3 to SnO_2 molar ratio of 1:1, 1:0.5, 1:0.2 and 1:0.1 were synthesized by sol-gel technique and characterized by thermal analysis and FTIR. In the case of binary gels – addition of tin component leads to better crosslinking than in pure alumina gel and as a result to a much uniform texture structure.

Keywords: *DTA, DTG, modified alumina, SnO_2, sol-gel*

Introduction

One of the advantages of the sol-gel preparation over conventional techniques is the possibility of controlling the porous structure of products. The variety of developed synthesis procedures, differences in the textural properties as well as structural changes caused by the high-temperature treatment indicate that organized mesoporous aluminas are interesting molecular sieve materials not only from the material science point of view, but also for the possibilities of their application, e.g. as supports in heterogeneous catalysis. In particular, the method of embedding various molecules through sol-gel processes has been of intense interest world-wide. In working on the development of new binary oxide supports for metal catalysts for industrial application, we have focused our attention on Al_2O_3–SnO_2 system prepared by sol-gel chemistry. Synthesis of mesoporous materials is a part of our broader investigation dedicated to comparative analyses of identical binary oxide systems obtained by sol-gel chemistry and by coprecipitation /impregnation preparation [1–3].

The majority of literature data on thermogravimetric studies of gel preparations have concerned silica gels or their binary modifications [4, 5]. Only a few authors have been interested in gel alumina [6–8] (and particularly in Al_2O_3–SnO_2 system) preparations and the main subject of their concern was the fragmentation (cracking) of gel monoliths on their thermal treatment in the aspect of applications in ceramic processes [9].

A large body of data have been published on thermal transformations of transition forms of alumina oxides and hydroxides taking place in specific conditions [10].

The aluminium hydroxide composition significantly depends on the conditions of its obtaining and the ageing period, as has been indicated already by Sato [11], who studied gel alumina obtained from water solution of its salts. Thermal analysis of such gels has proved that small changes in pH can lead to significant changes in the DTA curves explained as a result of dehydration.

For gel alumina preparations synthesized on the basis of alkoxide precursors, the character of the DTA curve is much more complex because the thermal effects related to dehydration are superimposed on the effects of pyrolysis of the organic residues captured in the gel lattice.

At this stage we would like to discuss the results of thermoanalysis of binary gel systems of Al_2O_3–SnO_2 in oxidative atmosphere.

Experimental

Preparation of the sol-gel binary samples

A support of the binary composition (Al_2O_3–SnO_2) with a molar ratio between 1:0 and 0:1 was synthesized by the sol-gel method worked out in our laboratory [12]. Briefly, as a precursor we used aluminum isopropoxide, tin(IV) acetate and as a moderator of the rates of hydrolysis and condensation (regulation of pH) acetic acid was added. For thermoanalysis we

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used both air-dried samples (room temp., 24 h) and those in which the encapsulated solvents were removed from the gel by evaporative drying followed by annealing at 373 K for 12 h.

Thermal analysis

Thermal transformation of the gel samples was carried out on a SETSYS 12 (Setaram – France) under the same conditions. A 20 mg sample was placed in alumina crucibles (volumes –100 mm^3) and heated at a rate 5 K min^{-1} up to 1273 K. For all experiments we used a fraction of the grain size between 100–200 Mesh. The TA-TG traces were recorded in air or helium atmosphere.

Fourier Transformed Infrared Spectroscopy (FTIR)

The infrared measurements were carried out in a home made quartz camera, which allows performing experiments in the range of pressures from 1–10^{-2} Pa. The gel films were placed in an IR cell equipped with heaters allowing their thermal treatment. The spectra were recorded at room temperature on a Brucker IFS88 FTIR Spectrometer in the 4000–400 cm^{-1} wavenumbers range.

Results and discussion

According to Iler [13], surface tension forces created in a gel during solvent removal cause the network to fold or crumple as the coordination of the particles is increased. Porosity develops when, due to additional crosslinking or neck formation, the gel network becomes sufficiently strengthened to resist the compressive forces of the surface. Thus, the dried xerogel structure is a contracted and distorted version of the structure originally formed in solution. It is worth adding that the above statement about the structure is valid for both skeletal and porous phases.

The most obvious physical change that occurs when an amorphous gel is heated above room temperature is its shrinkage. According to Brinker *et al.* [14] for a multicomponent gel the shrinkage curve could be divided into three regions defined by the accompanying mass loss. As expected all these regions are also visible in the binary sol-gel samples treated in air and helium alike atmosphere. The results of thermal analysis of simple alumina gel, both air-dried samples and those from which the encapsulated solvents were removed by evaporative drying followed by annealing at 373 K, are presented in Figs 1 and 2, respectively. In the case of air dried sample (Fig. 1) we are able to distinguish only two clear regions related to mass loss marked on DTG as I and III. The inflexion temperature determined from TG curve for the Ith mass lost falls to 357.6 K and the mass loss is equal to 11.2 mass%. This transformation as we can see from TA curve is endothermic and is attributed to desorption of physically adsorbed water and perhaps with residual solvent. This process of physically adsorbed water and that adsorption-desorption is reversible what confirmed by experiment with sample of alumina gel re-exposed to ambient conditions (~45% RH H_2O). In this special case, the samples of alumina gel after calcinations in air (6 h, 773.2 K) were exposed for air humidity for 1 h followed by thermal analysis in helium atmosphere. The result of this experiment is presented in Fig. 3. As we can easily see the mass loss related to the removal of physically adsorbed water falls almost at this same point as in Fig. 1 ($T_{\text{inflex.}}$=358.9 K); however, the corresponding mass loss is insignificantly lower and equal to 9.4 mass%. This could confirm our presumption about partial removal of residual solvent together with the water present in the gel network. Similar reversible adsorption-desorption process for silica xerogels has been reported Orgaz and Rawson [15]. The FTIR spectrum presented in Fig. 4 supports the above conclusion following from thermoanalytical experiments.

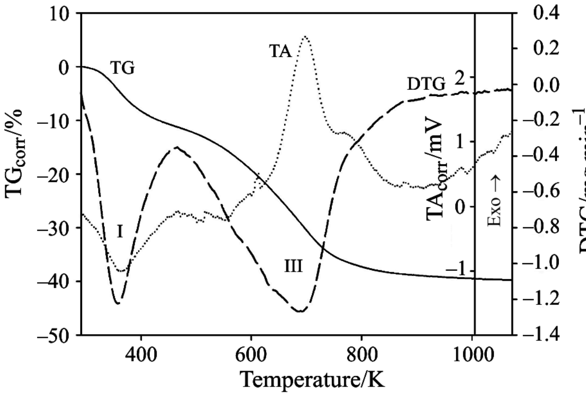

Fig. 1 TG-TA-DTG curves for alumina gel air-dried sample

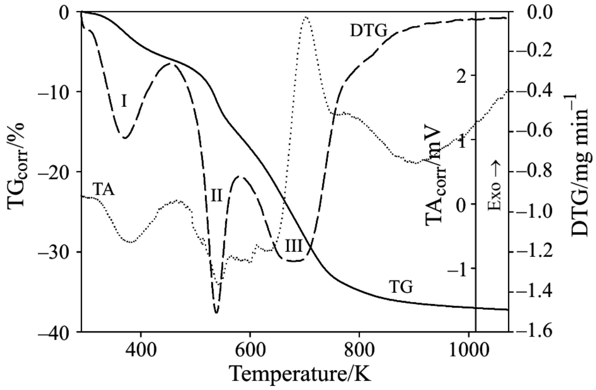

Fig. 2 TG-TA-DTG curves for alumina gel samples from which the encapsulated solvents were removed by evaporative drying, followed by annealing at 373 K

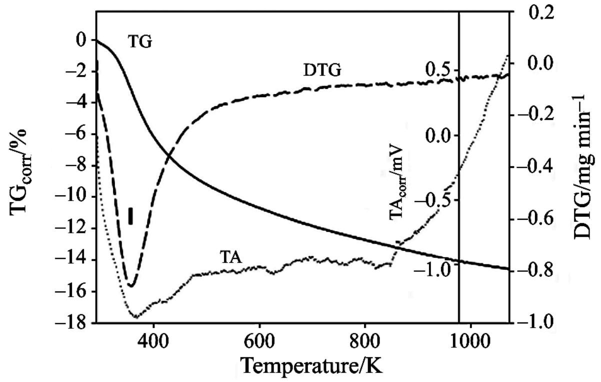

Fig. 3 TG-TA-DTG curves in helium atmosphere for alumina gel sample subjected to calcination in the air (6 h, 773 K) and followed by exposition to the air humidity for one hour

Temporary exposition of the previously calcined alumina (6 h, 773.2 K – spectrum a) film for air humidity (spectrum b) – leads to fundamental differences between these two spectra. In the FTIR spectrum of dehydrated and dehydroxylated surface of alumina gel (Fig. 4a) we are able to detect at least three separate bands assigned to the stretching vibration of the OH surface group. The re-exposition of the above film to the air humidity, even after its calcinations at 423.2 K (0.5 h, 10^{-3} Tr), does not lead to a disappearance of very broad unresolved band from the region corresponding to the OH stretching vibrations. It follows that secondary hydration of alumina gel (exposition to humidity) leads not only to the presence of physically adsorbed water, but also as a results of interactions of H_2O with unsaturated surface Lewis acid centres to a formation of whole spectrum of surface OH groups. The concentration of these surface OH groups leads to their association, which is reflected by a broad band in the region corresponding to stretching vibrations of OH group. The strong band at about 1640 cm^{-1} suggests that physically adsorbed water is present in the gel structure even after the above calcinations processes (423.2 K, 0.5 h, 10^{-3} Tr).

The second field connected with mass loss (denoted in the DTG curve as III Fig. 1) seems to be overlapping two processes, i.e. removal of organic substituents followed by exothermic oxidation over 673.2 K. Validation of the above statement is obtained from the experiment for the sample from which the excess of encapsulated solvent was removed from the gel by evaporative drying (at 373.2 K) – Fig. 2. In this case we can distinguish three very well separated 'band' corresponding to the mass loss denoted in the DTG curve as I, II, and III. The maximum of the removal rate of physically bonded water appears on DTG curve (I) at temperature a little higher than that for the air dried sample (Fig. 1) i.e. at 370.9 K with the corresponding mass loss equal to 5.7 mass%. The second maximum at $T_{inflex.}$=538.7 K (Δm=9.4 mass%) as we mentioned above is connected to endothermic carbonisation, whereas the maximum (III) at $T_{inflex.}$=675.4 K (Δm=21.2 mass%) prove the presence of exothermic oxidation organic residues. A comparison of Figs 1 and 2 rises a question why in the DTA curves obtained for air-dried samples (Fig. 1) we do not observe two separate 'bands' assigned to carbonisation (II) and oxidation (III), in contrast to the DTA curve obtained for the sample pre-treated at 373 K for 12 h (Fig. 2). The answer is undoubtedly related to a continue condensation reaction which, at the above conditions (373 K and 12 h), leads to creation of the inorganic skeleton in which organic residues are trapped.

The results of thermal analysis of the second component of the binary gel samples i.e. simple SnO_2 gel, are presented in Fig. 5. A comparison of the DTA and TA curves of alumina gel (Figs 1 and 2) with analogous results for SnO_2 gel (Fig. 5) reveals that in the curves of the latter there are no regions that could be assigned to endothermic carbonization (denoted as

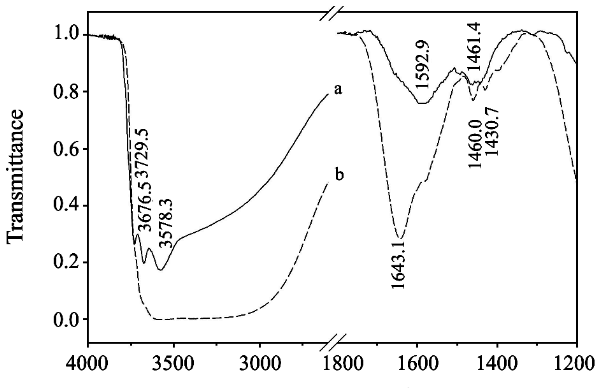

Fig. 4 FTIR spectra of a – alumina gel subjected to calcination in the air (6 h, 773 K), b – followed by exposition to the air humidity for one h

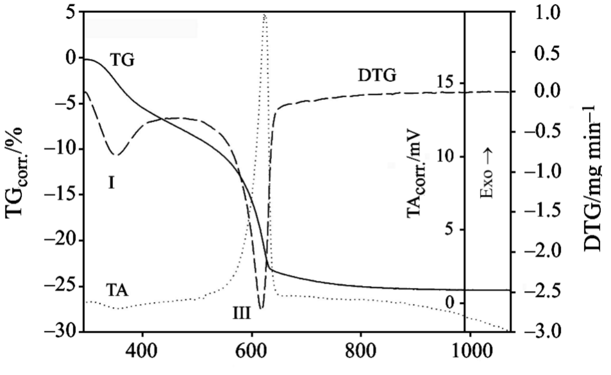

Fig. 5 TG-TA-DTG curves for SnO_2 gel air-dried samples from which the encapsulated solvents were removed by evaporative drying at room temperature

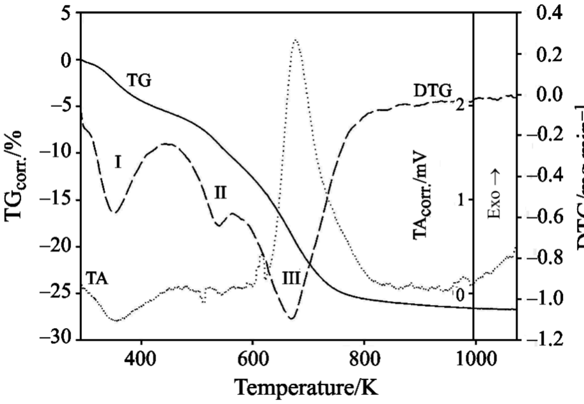

Fig. 6 TG-TA-DTG curves for Sn_g-0.1 gel air-dried samples with the encapsulated solvents removed by evaporative drying at room temperature

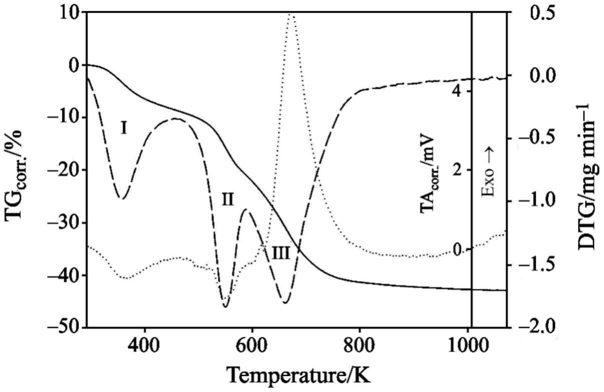

Fig. 7 TG-TA-DTG curves for Sn_g-0.2 gel air-dried samples with the encapsulated solvents removed by evaporative drying at room temperature

region II in Fig. 2). Additionally, the process of exothermic oxidation of organic substituents in SnO_2 gel not only takes place at a much lower temperature (T_{inflex}=618.93 K), but simultaneously it occurs with higher dynamic than in the alumina gel sample (in the case of alumina gel the exothermic oxidation spreads on the range of about two hundred degrees, whereas for SnO_2 this range is three times narrower. However, it is worth noting that in both samples (alumina and SnO_2) the process of combustion begins almost at this same temperature (at about 573 K). The above differences could suggest that in alumina the gel network is much stronger and more developed which straightforwardly leads to enhanced trapping of organic materials and as a consequence, more difficult mass transport in the bulk of the gel.

Taking into consideration the above suggestion, we did not expect that tin component will lead to improving property of crosslinking, however, as follows from the textural investigation [3], in a very broad range of tin concentration (from ~3–60 mass% i.e. up to ratio Al_2O_3:SnO_2 equal 1:1) the contribution of pores with almost the same range of diameters to the total volume of pores is more or less the same. According to the results reported in this paper, the main contribution to the total pore volume of this binary gel support comes from the pores of diameters ~1-4 nm, while in the sample of alumina gel, from the pores of diameters 2–10 nm. It seems to us that the results of thermal analysis of binary gel samples support the positive influence of tin additive on the structure of alumina gel samples. Figures 6 and 7 present the TG-TA-DTG curves for binary gel samples, i.e. the compositions with Al_2O_3:SnO_2 molar ratio of 1:0.1 and 1:0.2, respectively. As we can easily notice, the 'band' II for the sample Sn_g–0.1 ($T_{\text{inflex.}}$=538.16 K Δm= –4.9%) is much weaker than for sample Sn_g–0.2 ($T_{\text{inflex.}}$=549.5 K Δm= –12.3%), which suggests a better crosslinking in the latter one.

It is expected that the currently performed thermogravimetric study in the reducing atmosphere will answer the question why in the conditions simulating the reforming process (annealing at 773 K in hydrogen) the texture of the gel systems Al_2O_3–SnO_2 undergoes significant changes [3].

Conclusions

The process of physically adsorbed water is reversible both for pure alumina gel, as well as for binary gel samples (Al_2O_3–SnO_2).

In the case of mono component gels, the gelling process of alumina is more efficient in comparison to the corresponding one of mono component tin oxide gel.

In the binary gels – the incorporation of tin oxide leads to better crosslinking in comparison to that in pure alumina gel as well as to more uniform texture structure [3].

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