Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 1, 93–98

THERMAL ANALYSIS OF GEL-DERIVED SUPPORT FOR METALLIC CATALYST
Part II. Al_2O_3–SnO_2 system in reductive atmosphere

P. Kirszensztejn[1,2*], *A. Tolińska*[1] *and R. Przekop*[1]

[1]Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
[2]Faculty of Chemical Technology and Engineering, University of Technology and Life Science in Bydgoszcz, Seminaryjna 3
85-326 Bydgoszcz, Poland

A series of Al_2O_3–SnO_2 catalysts with the molar ratio of Al_2O_3 to SnO_2 between 1:0 and 0:1 have been characterized by thermal analysis in reductive conditions, TPR and XRD methods. In the reductive conditions in temperatures up to about 1000 K, no reduction of the tin component to the metallic form takes place in the binary gel Al_2O_3–SnO_2. In the temperatures characteristic of the reforming process, only a reduction to SnO occurs in the above binary support. Thermal analysis of the gels in the reductive conditions and TPR results indicate stabilisation of the tin oxide species even in the systems of the molar ratio of Al_2O_3 to SnO_2 of 1:1. The metallic tin appears in the binary gel only after its reduction in the hydrogen atmosphere at temperatures close to ~1100 K.

Keywords: *DTA, DTG, modified alumina, SnO_2, sol–gel, TG*

Introduction

Platinum–tin catalysts are very important reforming catalysts and their popularity seems to be ever growing [1, 2]. It is supposed that the addition of tin in the catalysts of reforming, based on the Pt/Al_2O_3 system, is responsible for stabilisation of the high degree of Pt dispersion on the surface of the oxide support. According to the generally accepted hypothesis, the formation of a surface layer of tin aluminate ($SnAl_2O_4$) is the direct reason for slowing down the process of thermal sintering of small metallic groups Pt [3–5]. This thin layer called by Davis [3, 4] the ‘egg shell of tin aluminate’ forms as a result of the interaction between the tin unreduced to the metallic state and the surface layer of alumina and is stabilised by this layer.

The above hypothesis is based on the results of a study of the system into which the tin component was introduced on the surface of alumina by impregnation. Thus, it can be assumed that usually the phase of tin aluminate was formed by the solid state interactions. The formation of the egg shell of tin aluminate is conditioned by the appearance of a tin precursor on the surface of alumina at the initial stage. In this context, of substantial importance becomes not only the type of the tin precursor applied at the initial stage of the catalyst preparation but also the method of preparation [6, 7].

Literature discussing the formation of $SnAl_2O_4$ is very poor. The only XRD data on $SnAl_2O_4$ synthesized by reacting SnO with Al_2O_3 at 1773 K have been reported by Spandau and Ullrich [8]. Taking into regard the temperature of the synthesis by almost 1000 K higher than that of the reforming process and the hypothetic existence of the above compound, it is rather unlikely that the above form is a consequence of simple interactions between tin oxides and the surface of Al_2O_3. It does not mean however, that the groups resembling stannic or stannous aluminate on the surface of alumina are excluded. Taking into regard the gelating abilities of tin(IV) compounds, the process of condensation of hydroxyl groups from the hydrolysed tin precursor (usually $SnCl_4$) with the hydroxyl groups on the Al_2O_3 surface can lead to formation of thin layer of binary gel that can hinder the migration of small metallic groups over the support surface.

Besides the above Davies’ hypothesis, increasing attention is paid to texture of the support. In other words, it seems that the immobilisation of small metallic groups (in our system Pt ones) on the surface of the support is also a result of textural matching [9]. These effects have been for the first time mentioned about in the middle of 20th century by Boreskov and Karnauchov [10] who studied chemisorption of hydrogen on platinum silica gels and found out that platinum occurs in these samples in the form of crystallites of the mean size of 5 nm equal to the diameters of the pores in silica gel. One of the approaches taken in order to explain the role of tin component in binary catalysts is based on synthesis of model systems by the sol–gel processes. In the above technology, the

---

* Author for correspondence: kirszen@amu.edu.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

products are devoid of inorganic impurities that could modify the physical and chemical properties of the support surface and the texture of the support surface can be controlled to a much greater degree, which can facilitate solving the problem.

The aim of this study was to compare the behaviour of binary gel systems of Al_2O_3–SnO_2 annealed in reductive condition with the results obtained in oxidative atmosphere [11].

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 (the notation Sn_g–0.2 refers to the composition where the molar ratio SnO_2:Al_2O_3 is 0.2:1) was synthesized by the sol–gel method worked out at in our laboratory [12]. Briefly, as a precursor we used aluminium isopropoxide, tin(IV) acetate and acetic acid was applied as a moderator of the rates of hydrolysis and condensation (regulation of pH). For thermal analysis we used both air-dried samples where the encapsulated solvents were removed from the gel by evaporative drying followed by annealing at 373 K for 12 h and the samples additionally calcined in air at 773 K for 6 h.

Methods

Thermal analysis

Thermal transformation of the gel samples was carried out on a SETSYS 12 (Setaram – France). A 20 mg sample was placed in alumina crucibles (volumes –100 mm^3) and heated at a rate 5 K min^{-1} up to 1400 K in the helium atmosphere or to 1273 K in the reduction atmosphere. The reductive atmosphere was achieved by blowing He containing 5 vol% of H_2 through the system. For the technical reasons (H_2 dissolves in the Pt components of the thermocouples) it was not possible to use pure hydrogen, as this would lead to erroneous results and damage to platinum elements. In all experiments we used the gel fraction of the grain size between 100–200 mesh.

X-ray diffraction analysis

The X-ray powder diffraction patterns of different samples were taken on a PW1050 diffractometer (made by Philips) with Ni-filtered CuK_α radiation. The APD Philips program calculated reflections position, half bandwidth as well as intensity. The objects of analysis were both samples exposed in air as well as samples after hydrogen treatment.

Temperature programmed reduction (TPR)

The thermally programmed reduction (TPR) study was performed in an instrument Micromeritics Pulse ChemiSorb 2705 with a TCD detector. Prior to the measurements the samples of gels were activated at 673 K for 1 h in the flowing helium atmosphere (25 cm^3 min^{-1}). Measurements were made from *RT* to 1400 K, with the temperature gradient of 10 K min^{-1}. During the measurement the reducing mixture of 5% (vol./vol.) hydrogen in argon was blown through the system at the rate of 40 cm^3 min^{-1}.

Results and discussion

In view of the fact that metallic catalysts are often used in conversion of organic products in the reductive conditions (e.g. catalytic reforming), the reduced dispersion of the metallic phase is related not only to the catalysts covering with carbon deposit but also to the changes in the surface morphology as a result of reduction processes. It is particularly important in the catalytic systems containing an easily reducible component such as SnO_2 in the bimetallic catalyst of reforming – Pt/SnO_2–Al_2O_3. Besides the chemical consequences such as formation of the alloys of Pt with Sn, also textural changes on the catalyst surface appearing as a result of the catalyst exposure in the reductive conditions, should be regarded.

On the basis of our previous studies [12] we have found that the hydrogen treatment of binary gel samples (Al_2O_3–SnO_2) changes the porous structure of such a system. It should be noted that the nature of these changes is different than in the parallel-co-precipitated system (not to mention the analogous systems to which tin component was introduced by impregnation). It was expected that the thermal analysis would help understand the mechanisms of the textural transformations.

As follows from our previous studies [11] by TG-DTG-DTA (in helium atmosphere) of pure alumina gel after re-exposition to ambient conditions (sample of gel after calcination in air for 6 h, 773.2 K was exposed for air humidity), besides the mass loss related to the removal of physically adsorbed water (falls almost at this same temperature as for alumina gel air-dried sample $T_{\text{inflex.}}$=358.9 K) no additional mass changes were noted.

As shown in Figs 1–3, (TG-DTG-DTA-He Sn_g–0.1 Sn_g–0.2 and Sn_g) the re-exposition of binary gel systems to the ambient conditions gives the TG-DTG-DTA curves similar to those obtained for pure alumina gel [11]. The only difference, notable for the gels with a great contribution of the tin component, is the appearance of a small maximum on the DTG curves (Fig. 2) at 757 K. In the case of tin,

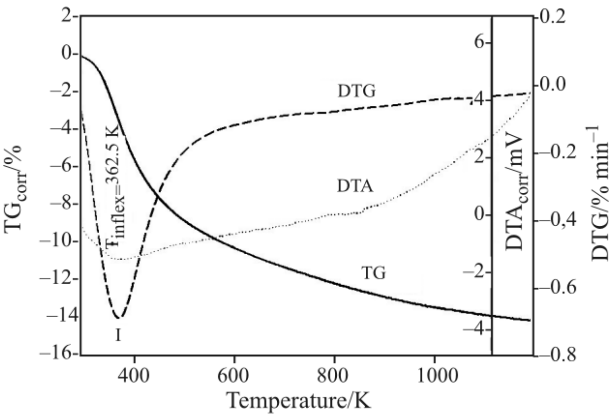

Fig. 1 TG-DTG-DTA curves in helium atmosphere for Sn_g–0.1 gel sample subjected to calcination in the air (6 h–773 K) followed by exposition to the air humidity for 1 h

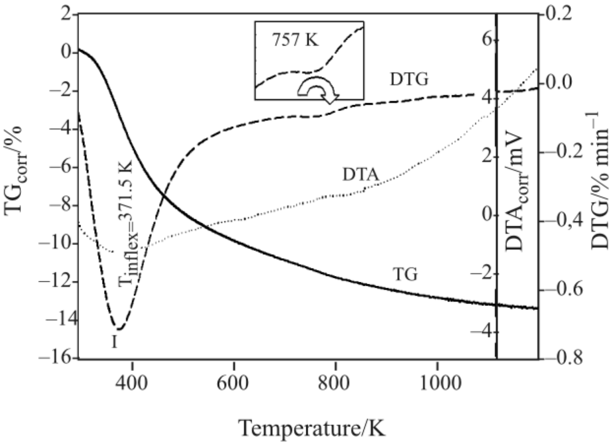

Fig. 2 TG-DTG-DTA curves in helium atmosphere for Sn_g –0.2 gel sample subjected to calcination in the air (6 h – 773 K) followed by exposition to the air humidity for 1 h

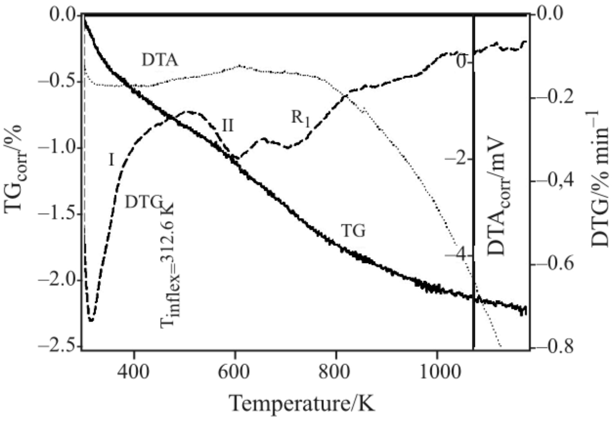

Fig. 3 TG-DTG-DTA curves in helium atmosphere for pure Sn_g gel sample subjected to calcination in the air (6 h–773 K) followed by exposition to the air humidity for 1 h

IV state is more stable than II, but the energy difference between the two oxidation states is quite small. Hence, for tin dioxide exposed at higher temperatures in the absence of oxygen (for example vacuum, inert atmospheres) we could expect processes leading to formation of non-stoichiometry of the form $SnO_{(2-x)}$ in the bulk of the sample or formation of oxides form on lower oxidation state. With regards to the above we could conclude that the above small maximum is connected to this processes.

On the basis of a comparative analysis of mass loss related to the removal of physically adsorbed water (fragments denoted as I on TG-DTG-DTA figures) performed for a series of gel preparations, it has been concluded that an increase in the content of tin in the binary system does not change significantly the amount of the physically adsorbed water (10.1 and 11.6 mass% for Sn_g–0.1 and Sn_g–0.2, respectively) and it remains almost the same as for pure alumina gel (11.2 mass%). It should be noted that the temperature at which the water desorption is the fastest has been only slightly changed towards higher values with respect to that obtained for pure aluminium gel. This shift oscillated within 10 K, irrespective of the content of the tin component. Only for the pure SnO_2 gel (Sn_g sample) foregoing mass loss has dropped down to 0.8 mass% from about 11.2 mass% for pure alumina gel [11]. This decrease in the sorption capacity seems obvious taking into regard the surface area of the preparations compared (S_{BET} for Sn_g, Sn_g–0.1 and Sn_g–0.2 are 26.1, 311.1 and 323.4 m^2 g^{-1}, respectively). The temperature of water evacuation for pure tin gel Fig. 3 much lower (almost by 50 K) than that for pure alumina gel and its binary compositions is most probably a consequence of two factors. The first and most important factor reducing the time of water retention is the low amount of water readsorbed on the surface of tin gel. On the other hand, poorly developed texture of tin gel means that the physical adsorption of water mainly occurs onto its plane surface and not inside the pores, which also facilitates its removal from the surface. In other words, we can exclude all processes connected to capillary condensation. It does not seem justified enough that the addition of tin into the structure of the binary alumina gel would change the electronic interactions between Sn and Al in the structure of the gel towards increasing the effect of Al polarisation and enhancement of the London type interactions of water with the alumina gel surface. The reverse, that is an increase in the interaction forces between water and surface is true in the binary gel system $MgO–Al_2O_3$ [13].

The two small mass loss events observed on the DTG (Fig. 3) of pure tin gel in the helium atmosphere (Δm~ –0.4 mass%) with the maxima at 608 and 705 K

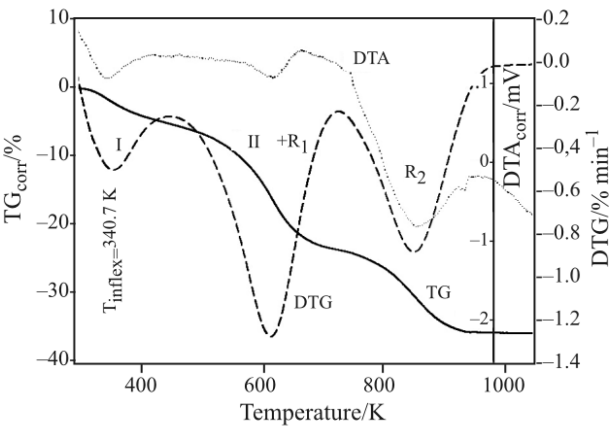

Fig. 4 TG-DTG-DTA curves in the reductive atmosphere for pure Sn_g gel sample from which the encapsulated solvents were removed by evaporative drying, followed by annealing at 373 K for 6 h

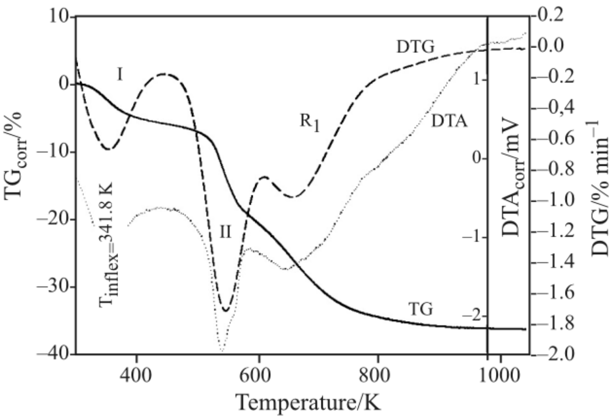

Fig. 5 TG-DTG-DTA curves in the reductive atmosphere for pure Sn_g–0.1 gel sample from which the encapsulated solvents were removed by evaporative drying, followed by annealing at 373 K for 6 h

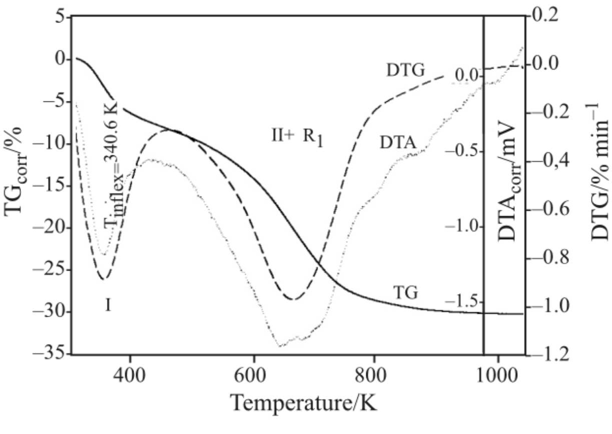

Fig. 6 TG-DTG-DTA curves in the reductive atmosphere for pure Sn_g–0.2 gel sample from which the encapsulated solvents were removed by evaporative drying, followed by annealing at 373 K for 6 h

are assigned to the carbonisation of small amounts of organic remains in the gel lattice and the transformation of SnO_2 to $SnO+1/2O_2$. The total removal of the organic remains encapsulated in the gel lattice requires their annealing at 880 K for at least 12 h in the oxygen atmosphere, as proved by the FTIR study of a thin gel film of 0.5 mm in thickness. Changes in the course of the analogous DTG curves recorded in the reductive atmosphere (5 vol.% H_2 in He) for dry gels (prior to analysis dried at 373 K for 12 h) are shown in Figs 4–6. Similarly as for the analogous study in the oxidative atmosphere [11] in the range to ~400 K the mass loss is related mainly to the removal of water and volatile organic impurities not built into the gel lattice. As expected, the character of the DTG profiles and the parameters (Δm, T_{inf}) are similar for the curves recorded in the reductive and oxidative atmosphere. Interpretation of the results obtained in higher temperatures is much more complex. The DTG curve for pure tin gel has two characteristic fragments. The first marked by R_1 (614.5 K $\Delta m = -18.4$ mass%) in Fig. 4, can be related to reduction of SnO_2 to SnO. However, the mass loss seems too high (18.4 mass%), almost twice higher than the theoretically predicted for SnO_2 reduction to SnO (10.6 mass%). A reasonable explanation is that this high mass loss is a result of a combined effect of two endothermic processes that is the above reduction (R_1) and carbonisation (II) of the organic impurities present in the gel [10]. The maximum observed for the process taking place in the reductive conditions (614.5 K) can be assigned to similar processes in the helium atmosphere at 608 and 704 K. As expected, the mass loss accompanying these transformations in the helium atmosphere is much lower (Fig. 3). It is a consequence of the fact that the analysis was made on the sample preliminary calcined in the air atmosphere at 773 K for 6 h, on the other hand the only factor initiating the decomposition of tin(IV) oxide in the atmosphere devoid of oxygen is the thermal equilibrium SnO_2/SnO. Near 800 K another interesting fragment of the curve appears (R_2) with a maximum at 856.8 K, assigned to the reduction to metallic tin.

The calculations made taking into account all mass losses on the DTG curve (occurring before the fragment denoted as R_2) and assuming that the fragment denoted as R_1 corresponds to the reduction of SnO_2 to SnO, indicate that the fragment denoted as R_2 corresponds only to the reduction of SnO to metallic tin.

Similarly as for pure tin gel (Fig. 4) also for the binary systems (Figs 5 and 6) the DTG curves show endothermic maxima in the range 450–700 K, interpreted as manifestations of the carbonisation of the organic impurities present in the gel lattice and the following process of reduction to SnO. With increasing tin component contribution, the temperatures of these two processes overlap (Fig. 6). It should be noted that the reduction to SnO in the binary system occurs at a temperature by about 40 K higher than in the pure tin gel. In the binary systems in the range from *RT* to 1000 K, in the reductive atmosphere, the reduction to metallic tin has not been observed. This fact has confirmed our supposition about the stabilisation of the oxidised tin species in the matrix of alumina gel [12].

TG-DTG-DTA results were verified by the thermally programmed reduction measurements (TPR) of the binary gel system and pure tin gel. This method enables determination of changes in the sample mass in the hydrogen atmosphere (5 vol% H_2 in Ar) up to 1400 K so by 400 K higher temperature than in the DTA study. Figure 7 presents the TPR courses revealing changes corresponding to the reduction of the systems Sn_g–0.1 and Sn_g–0.2, with respect to the TPR of the pure tin gel Sn_g. For the pure tin gel, the TPR profile shows two maxima at 718 and 912 K, assigned to the reduction of tin. The first one corresponds to the reduction of SnO_2 to SnO, whereas the other one to the reduction to the metallic form. Because of the differences in the detection techniques, the sensitivity of the instruments and the size of the samples used for the study by these two methods, we did not expect to get the same temperatures of reduction determined by the two methods. Much more important was to get the agreement between the TPR and DTG profiles. Taking into regard the fact that the DTG profiles show the mass changes corresponding to all processes not just those of reduction of the tin component, (e.g. carbonisation), the TPR results confirmed our conclusions drawn from the DTA study. In particular, the TPR results supported the hypothesis of the stabilisation role of the tin oxide species in the binary gel with Al_2O_3. On the basis of the maxima appearing near 1100 K and assigned to the reduction of tin oxide species to the metallic form, it can be concluded that in the binary systems this process takes place at a temperature over 200 K higher than that in the pure tin gel ($T_{reduc.}$=912 K).

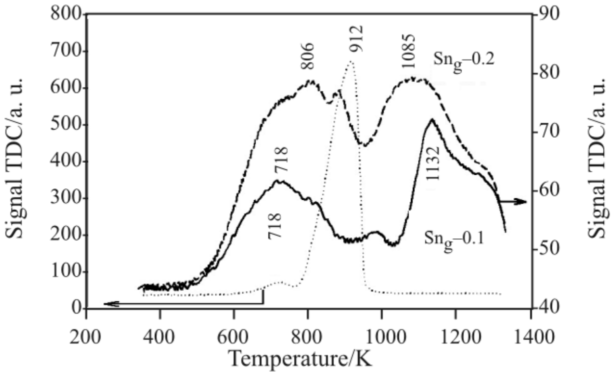

Fig. 7 Temperature programmed reduction of gel samples

Figure 8 presents the XRD patterns of binary systems taken after their reduction in the hydrogen atmosphere at 773 K (6 h). Prior to the reduction all samples were calcined in the air atmosphere also at 773 K for 6 h. For comparison, Fig. 8a presents also the XRD pattern of Sn_g–0.2 sample calcined in the air. For alumina no reduction processes are expected at this temperature. In view of the fact that the XRD pattern of alumina (annealed in the hydrogen atmosphere) can be a useful reference in interpretation of the XRD data of its binary systems, it is presented in Fig. 8b. Another argument is that the XRD pattern of xerogel of alumina annealed in the air atmosphere is identical to the XRD pattern of the sample subjected to additional 6 h annealing at 773 K. This result means that the twice increase of the time of annealing has not led to formation of a more developed crystalline phase.

In general, a characteristic feature of the XRD patterns obtained for the binary systems, irrespective of the atmosphere of calcination, is the disappearance of the reflexes from the γ-Al_2O_3 phase, being a consequence of introduction of the tin component to the alumina gel. This observation points to the inhibiting role of the tin component in the processes of crystallisation of this binary system. Only in the samples with high loading of tin component (Sn_g–0.5 and Sn_g–1.0 calcined in air, where concentration of

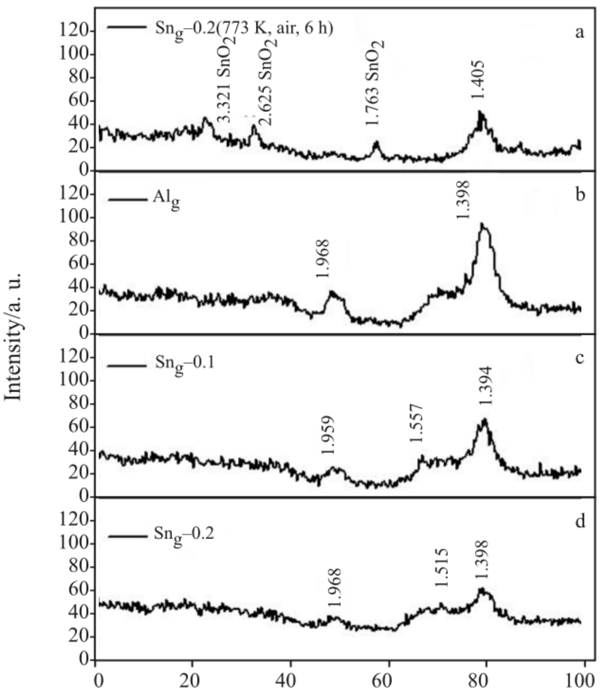

Fig. 8 XRD pattern for binary gel samples annealed in hydrogen atmosphere at 773 K for 6 h. For comparison, Fig. 8a presents also the XRD pattern of Sn_g–0.2 sample calcined in the air

SnO_2 in gel sample is of about 42 and 60 mass/mass%, respectively) some reflexes assigned to SnO_2 could be detected, however, slightly shifted to smaller values of *d* which could suggest that alumina ions are incorporated into the casseterite structure. It is also partly visible for the sample Sn_g–0.2 calcined in air (Fig. 8a). As it is easily visible when comparing Fig. 8a with Fig. 9d, the annealing in hydrogen atmosphere leads to the disappearance of the reflexes assigned to cassiterite. It should be noted that the above treatment did not lead to the appearance of any new phase. Taking into consideration that in such conditions pure tin dioxide could be reduced to metallic tin, it is reasonable to assume that the inhibition of phase separation, crystallisation or reduction of the tin component to the metallic form is the responsibility of the strong Sn–O–Al bonds forming the gel network structure. The lack of the reflexes corresponding to the presence of metallic tin in binary gel preparations after their exposition to hydrogen is particularly important from the point of view of their application as a Pt support in the catalysts of reforming. The metallic form of tin, present on the surface of the catalyst, will dissolve metallic Pt leading to formation of a wide spectrum of alloys (PtSn, Pt_3Sn, etc.) and as a result, Pt will lose its dispersion and the catalyst its activity.

Conclusions

A characteristic feature of gel-derived systems Al_2O_3–SnO_2, irrespective of the atmosphere of annealing, is a distinct reduction of the reflexes intensity from the γ-Al_2O_3 phase, being a consequence of introduction of the tin component to the alumina gel. This observation points to the inhibiting role of the tin component in the processes of crystallisation of this binary system. In the range of temperatures, characteristic for reforming conditions, we do not observe process of reduction of tin component to the metallic form. For samples with high loading of tin component after calcinations in oxidative conditions some reflexes on the XRD pattern assigned to the SnO_2 could be detected, however, slightly shifted to smaller values of *d*, which could suggest that alumina ions are incorporated into the casseterite structure. Annealing in reductive conditions leads to the disappearance of the above reflexes and does not lead to the appearance of any new phase. In regard to the fact that in such conditions pure tin dioxide is reduced to metallic tin, it is reasonable to assume that the inhibition of phase separation, crystallisation or reduction of the tin component to the metallic form is the responsibility of the strong Sn–O–Al bonds forming the gel network structure. On the basis of DTA curve taken in the reductive conditions we have found that the process of tin oxide reduction to metallic tin in the binary system occurs at a temperature by about 200 K higher than in the pure tin gel which support our previous statement on the XRD investigation.

Acknowledgements

We gratefully acknowledge the financial support given by the Minister of Science and University Education within the research project no. N204 068 31/1847.

References

1 F. M. Dautzenberg, German Offenlegunsschrift, 2,121, 763 (1971).
2 S. Toppi, C. Thomas, C. Sayag, D. Brodzki, K. Fajerwerg, F. Le Peltier, C. Travers and G. Djega-Mariadassou, J. Catal., 203 (2005) 255.
3 R. Srinivasan, R. J. De Angelis and B. H. Davis, J. Catal., 106 (1987) 449.
4 S. R. Atkins and B. H. Davis, J. Catal., 89 (1984) 371.
5 K. Balakrishnan and J. Schwank, J. Catal., 138 (1992) 491.
6 B. Pacewska, O. Kluk-Płoskońska and D. Szychowski, J. Therm. Anal. Cal., 87 (2007) 383.
7 B. Pacewska, O. Kluk-Płoskońska and D. Szychowski, J. Therm. Anal. Cal., 90 (2007) 783.
8 H. Spandau and T. Ullrich, Z. Anorg. Chem., 274 (1953) 271.
9 P. Kirszensztejn, A. Szymkowiak, R. Przekop and E. Maćkowska, Pol. J. Environ. Stud., 15 (2006) 74.
10 K. Boreskov and A. P. Karnauchov, ŻFCh., 26 (1952) 26.
11 P. Kirszensztejn and A. Szymkowiak, J. Therm. Anal. Cal., 81 (2005) 35.
12 P. Kirszensztejn, A. Szymkowiak, P. Marciniak, A. Martyła and R. Przekop, Appl. Catal. General A, 245 (2003) 159.
13 P. Kirszensztejn, R. Przekop, A. Szymkowiak, E. Maćkowska and J. Gaca, Micropor. Mesopor. Mater., 89 (2006) 150.

Received: March 1, 2008
Accepted: April 3, 2008
OnlineFirst: August 15, 2008

DOI: 10.1007/s10973-008-9085-0