

CALCINATION OF SiO₂-AEROGEL IN OXIDIZING ATMOSPHERE

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(Received January 13, 1998; in revised form April 14, 1998)

Abstract

Differences in mass loss occurring in the course of dynamic and isothermal heating of SiO₂-aerogel and changes of specific surface and hydrophylicity during calcination were studied by thermal analysis. SiO₂-aerogel was prepared from tetramethoxysilane (TMOS) hydrolyzed by ammonia solution at 0°C with molar ratio TMOS: H₂O:NH₄OH 4:1:0.01. Differences are caused mainly by oxidation of organic matter and by diffusion of products of the oxidation. Heat transfer has none or little effect on the differences. Samples calcined at temperatures about 300°C reach maximum hydrophilicity though they still contain small amounts of residual organic matter.

Keywords: aerogel, calcination, hydrophylicity, TG

Introduction

Due to their extreme porosity and unusual pore size distribution, inorganic aerogels have very interesting properties. That is why aerogels have applications in high energy physics as Cherenkov radiation detectors, in optics and in thermoinsulation technique as well.

Calcination of SiO₂-aerogel in oxidizing atmosphere is the terminal step during the preparation of SiO₂-aerogels and the conditions under which this process is carried out have great effect on the properties, for example on the porosity and specific surface. Both porosity and specific surface can be affected in the course of preparation of alcogel [1-4] as well as during calcination of aerogel after supercritical drying [5-7]. In contrast to the high-temperature calcination of SiO₂-aerogel, which is extensively described in chemical literature [5-7], the problem of low-temperature calcination is mostly reduced to the statement that the process of hydrophilization is caused by the release of terminal CH₃-O- groups.

This paper deals with the problems of the kinetics of release of organic matter from SiO₂-aerogels and with a detailed study of the effect of calcination temperature on the hydrophilicity of calcined SiO₂-aerogel.

Experimental

SiO₂-aerogel was prepared from tetramethoxysilane (TMOS, Fluka puriss., >99% by GC) which was hydrolyzed by a water solution of ammonia, serving as a basic catalyst, at a temperature of 0°C. The molar ratio of TMOS:H₂O:NH₄OH was 4:1:0.01. Prior to hypercritical drying the alcogel had undergone a 7-day aging at ambient temperature during which the structure of alcogel was hardened. For the hypercritical drying a stainless steel autoclave with a volume of 1 dm³ was used. Alcogel samples in teflon cylindrical vessels with a diameter of 3 cm and height of 3 cm were placed in the autoclave immersed in methanol. Before heating, the autoclave was thoroughly flushed with argon and then pressurized to 4 MPa as starting pressure. The heating rate was 15°C h⁻¹ up to 270°C and then, at constant temperature the methanol vapour was slowly released to the atmospheric pressure. Then the temperature was slowly lowered (cooling rate 30°C h⁻¹). The maximum pressure during synthesis was 12 MPa.

The density of SiO₂-aerogel prepared under the above described conditions is 0.19 g cm⁻³. The aerogel was crushed and sieved and for further experiments only the fraction between 0.5 and 1.0 mm was used. Six samples were prepared from aerogel granulate by annealing at 100, 400, 500, 600, 700 and 800°C, respectively.

Physical sorption of nitrogen was measured by a Soptomatic 1900 (Erba Science) equipment at the temperature of liquid nitrogen -197°C. The specific surface area was determined by means of the BET method in the range of $p/p_0=0.05-0.30$, the pore size distribution was calculated by the BHI method from the desorption part of the isotherm.

Curve a in Fig. 1 is based on mass loss of one sample during the isothermal heating (12 h) at the temperatures 100, 200, . . . 800°C, respectively. The amount

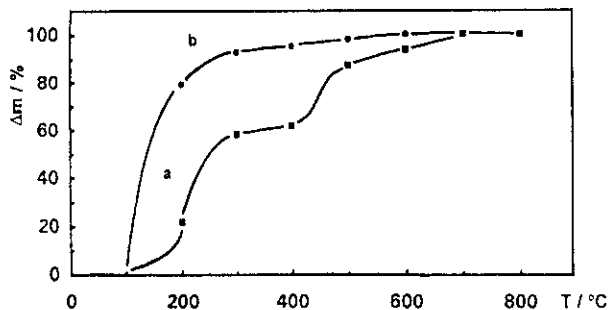


Fig. 1 Mass loss of SiO₂-aerogel (curve a) and loss of carbon (curve b) in the same sample during calcination. Mass of sample 500 mg

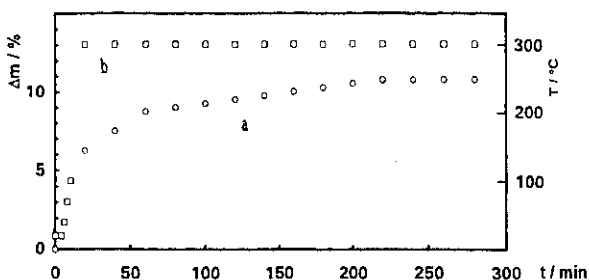


Fig. 2 Mass loss of a granulated sample of SiO₂-aerogel (40 mg) vs. time of heating (a – mass loss, b – sample temperature)

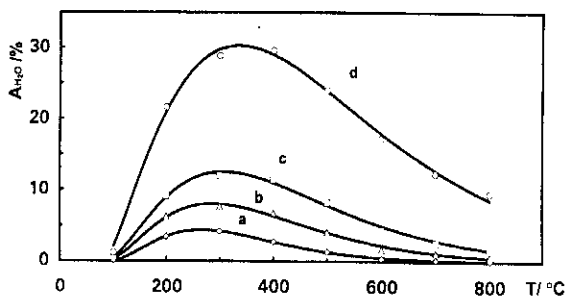


Fig. 3 Temperature dependence of the amount of water absorbed on SiO₂-aerogel samples at different relative water vapour pressures p_r , a – $p_r=0.3$, b – $p_r=0.5$, c – $p_r=0.7$, d – $p_r=0.9$

of carbon in the samples (Fig. 1, curve b) was determined by Carlo Erba 104 CHN analyser. The curves in Fig. 2 are based on thermogravimetric and temperature measurements carried out on a Derivatograph OD 102, MOM, Budapest, Hungary. The amount of water vapour absorbed by the aerogel in equilibrium was measured by gravimetry (Fig. 3).

Results and discussion

The mass loss of the sample during a long time isothermal heating at temperatures from 200 to 800°C is shown in Fig. 1 (curve a). The mass loss of the sample occurs in two steps. While the unbonded organic matter is released already at 200°C, the main mass loss of the sample is finished by the temperature of 300°C (Fig. 1 curve b). The main fraction of CH₃-O- groups bonded to the SiO₂ net of the aerogel is released in the temperature interval 200–400°C.

During a dynamic heating of SiO₂-aerogel in an air atmosphere, described in [8], two main processes can be seen in the TG curve – evaporation of methanol (60–80°C) and gradual release of residual water molecules (up to 260°C). CH₃-O- groups are released in two steps and the process is accompanied by the combus-

tion of the reaction products of CH₃-O- groups. The corresponding exothermic peaks in the DTA curve have maxima at 320°C and 440–460°C. The last process is a slow continuous dehydroxylation of SiO₂-aerogel in the temperature interval 800–1000°C.

The differences in the position of maxima between the DTG (DTA) curve in [8] and mass loss in the curve in Fig. 1, corresponding to the combustion of organic matter (320 and 450°C), may be caused by the high heating rate and the high mass of sample used during the TA in [8]. Delayed sample heating in the whole mass of sample during the dynamic heating, caused by the low thermal conductivity at these temperatures, should shift the positions of corresponding peaks to higher temperatures. But heat transfer through the heated aerogel sample has no significant effect on the duration of aerogel calcination as it can be seen in Fig. 2 (temperature was measured in the middle of the powdered sample, 40 mg). A shift of peak maximum during dynamic sample heating then should be caused by diffusion of the decomposition products of the organic matter in the aerogel sample.

The change of water vapour absorption capacity in dependence on the calcination temperature is presented in Fig. 3. The maximal increase in aerogel hydrophilicity is observed in the temperature interval 100–200°C where the aerogel still contains chemically bonded methoxy groups. This increase is more pronounced at higher relative water vapour pressures when capillary sorption occurs. Removal of methoxy groups causes further increase in the sorption capacity of the aerogel. The SiO₂-aerogel samples reached maximum hydrophilicity when calcined at a temperature of about 300°C. At this temperature there are still residues of organic matter in the aerogel sample. This is not in accordance with values of the specific surface, which increases up to the temperature of 600°C (Fig. 4). At lower temperatures a decrease in sorption capacity is caused by dehydroxylation of the surface and at temperatures over 600°C by vitrification of the SiO₂-aerogel.

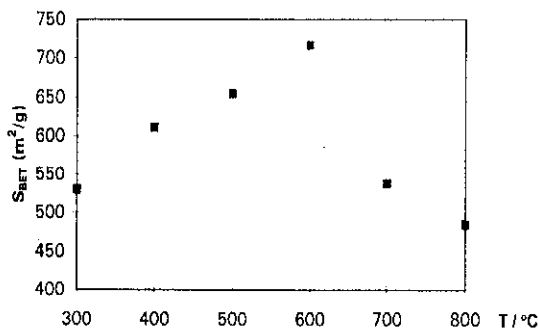


Fig. 4 Dependence of specific surface area of SiO₂-aerogel on calcination temperature (specific surface area measured by nitrogen adsorption)

Conclusions

Thermal analysis is suitable for identification and analysis of processes occurring in the course of SiO₂-aerogel calcination. Although the thermal conductivity of the aerogel is extremely low, the differences in mass loss measured during dynamic and isothermal heating of SiO₂-aerogel samples cannot be explained by heat transfer through the sample measured under common conditions. Calcination temperature should differ according to whether the aim is to get a sample with maximum specific surface or with maximum hydrophilicity. The reasons for these differences in calcination temperature are not known yet.

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The authors would like to thank the Slovak Grant Agency for financial support of project No. 1/2170/95.

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