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ABOUT THE SYNTHESIS AND THERMAL STABILITY OF SiO_2–AEROGEL

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Abstract

Aerogels are extremely porous high-tech materials based on inorganic oxides, especially silica. The paper describes synthesis and properties of SiO_2–aerogel, and changes occurring during heating of SiO_2–aerogel in the temperature range from 20 to 1000°C. Four thermoanalytical methods were used: Thermodilatometry, Differential thermal analysis, Thermogravimetry and Derivative thermogravimetry.

Keywords: SiO_2–aerogel, synthesis, thermal stability

Introduction

Aerogels are materials of extreme porosity and very low density. In most cases they consist of inorganic oxides such as SiO_2, Al_2O_3, ZrO_2, TiO_2, WO_3 or a mixture of these oxides. Aerogels have large surface area ($\approx 10^3\ m^2\ g^{-1}$) and can be translucent as well as transparent, have extremely low thermal conductivity ($<2\cdot10^{-2}\ W\ m^{-1}\ K^{-1}$), and have fascinating acoustic properties (sound velocity as low as $10^2\ m\ s^{-1}$).

Porosity of aerogels amounts to 85–99.8%. It means that in their volume there is more air than solid, and they smoothly fill the density gap between the "heaviest" gases and the "lightest" liquids. In other words, there is no substance of aerogel density in the nature. Specially prepared aerogels have a density of approximately 5 $mg\cdot cm^{-3}$ (only about four times higher than the density of air at normal conditions).

Aerogels

Aerogels are coherent porous solids that are prepared by formation of a colloidal gel and subsequently by removing the liquid from the pores. Despite the fact that Kistler [1–4] prepared the first aerogel as far back as 1931, they were not practically used up to the seventies [5].

Progress in the preparation technique and detailed study of these materials was stimulated in the mid-seventies by their possible use as liquid propellant

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carriers [6, 7], special highly effective catalysts [8, 9] and radiators in Cherenkov detectors for high-energy particles [10–13].

Later the aerogels were used as reliable heat insulators in the so-called "supra-windows" [14–16] and they are also promising as filter materials, especially for separation of aerosol–gas mixtures [17]. The advantages of aerogels as filters are that they are temperature resistant up to 500°C and have pores which can be "tailored" in the range of about 10–100 nm, either in the sol-gel process or by sintering [18].

Recently few detailed review papers appeared on this subject [19–25]. In 1990 the aerogels were listed [26] among ten most promising themes of investigation in science and technology in the USA.

Synthesis of aerogels

Preparation of aerogel can be divided into two steps. The first step – creation of alcogel – is a chemical process and the second one – transformation of alcogel to aerogel – may be supposed as a physical process.

The preparation of alcogel has undergone great changes since the first aerogel was prepared by Kistler [1]. Kistler chose "water glass" as a starting material and let it to react with hydrochloric acid. The solution of prepared silicic acid was then let "hardened" for 24 h in paraffined crystallizing dishes. Afterwards, the gel was placed in water and rinsed until the water showed no chloride ions. At the end of this process water in the gel was substituted by 95% alcohol [2–4].

A great improvement in this process was made by Teichner and co-workers about 30 years ago [6]. They prepared alcogel from tetramethoxysilane dissolved in methanol and hydrolysed it by a controlled amount of water:

$$Si(OCH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3OH$$

As no impurities were formed, long tedious washing of the gel was not necessary and because of using alcohol as initial solvent no substitution of the solvent was needed [27]. The process is usually catalysed by acidobasic reactions. The acid and base catalysis have different effects on the ratio between hydrolysis and condensation velocity. In the case of the acid catalyst the condensation tends to start in a later stage, whereas the basic catalyst condensation starts relatively early. The acid catalysis leads to a more polymeric type of gel with linear chains as intermediates [28]. Gelation then occurs by crosslinking. Base catalysis leads to so-called colloidal gels [29, 30].

Transformation of alcogel to aerogel has to be done under special conditions – so-called hypercritical drying – otherwise the extremely fine structure of aerogel would be destroyed by capillary forces. Alcogel placed into an autoclave and sunk in alcohol is very slowly heated and only when the critical temperature is overcome, vapours of alcohol can be slowly released.

Using only the hypercritical drying, the aerogel is hydrophobic and very fragile. That is why the product is usually annealed at the temperature 400°C or higher but during this process besides the hardening a loss of hydrophobicity and some shrinkage occurs. When chemicals with very high purity are used and the temperature during alcogel synthesis is kept low, final SiO_2–aerogel is transparent with only a weak opalescence.

Experimental

Materials

Tetramethoxysilane (FLUKA, puriss., >99% by GC) was used for preparation of alcogel. As basic catalyst 25% water solution of ammonia (LACHEMA, p.a., Czech Republic) was used.

Equipments

DTA and DTG measurements were carried on the Derivatograph OD-102 (MOM Budapest) – heating rate 600°C h^{-1}; weight of sample 50 mg; atmosphere air, static. For dilatometric measurements dilatometer NETZSCH–402 E with heating rate 600°C h^{-1} was used.

Method of preparation

At our department SiO_2–alcogel is synthetized from tetramethoxysilane (TMOS) which is hydrolysed by a water solution of ammonia serving as basic catalyst at the temperature 0°C. The used molar ratio of TMOS : H_2O : NH_4OH is 4 : 1 : 0.01. Prior to hypercritical drying the alcogel undergoes 7-day aging at ambient temperature during which the structure of an alcogel is hardened. For the hypercritical drying we use a stainless steel autoclave (1 dm^3). Alcogel samples in teflon vessels of different shape and size are in the autoclave sunk in methanol. Before heating the autoclave must be thoroughly flushed with argon to avoid an explosion of methanol vapours and then is pressurized to 4 MPa as starting pressure. Heating rate is 15°C h^{-1} up to 270°C and then the temperature is kept constant while alcohol vapours are slowly released to the atmospheric pressure. Then temperature is slowly lowered (cooling rate 30°C h^{-1}). Maximum pressure is 12 MPa. Temperature in autoclave is controlled by PC computer.

Density of SiO_2–aerogel prepared under conditions described above is 0.19 g cm^{-3} and refractive index is 1.040.

Results and discussions

Thermal analysis

The most used thermoanalytical method for the study of SiO_2–aerogel is thermodilatometry. But the differential thermal analysis (DTA) and thermogravimetry (TG) are used also for the thermal study of SiO_2–aerogel.

Dilatometric behaviour

From the results obtained by different authors [31–33] as well as results from our measurements following can be deduced: In temperature range from 20 to 200°C no dimension change of SiO_2–aerogel sample occurs. From this temperature to 500°C the aerogel sample is slowly and progressively shrinking (about 1% of length). Above 600°C the shrinkage becomes distinctive and can achieve values 30–40% depending on sample handling before the measurement or on the heating rate during the measurement. Density of the sample is increasing proportionally to the change of dimension (volume) of the sample while the specific surface is decreasing. During our thermodilatometry measurements the specific surface of SiO_2–aerogel samples decreased to one third of the initial value and the density increased to 0.35 g cm^{-3}.

Thermal decomposition

When oxidizing atmosphere is used (to avoid carbonization of organic matter) all processes occurring during the heating of the sample can be divided into three temperature intervals. The release of water absorbed at the surface of aerogel and the release of residual alcohol, occurring between 20 and 250°C, belong both to the first step (Δm 2–3%). Oxidation of the alcoxy groups (methoxy or ethoxy groups) above the temperature 275°C is manifested by more or less distinct exothermic peaks on the DTA curve [34–36] and it is accompanied by the sudden weight loss which depends on the mode the aerogel was prepared. Our SiO_2–aerogel samples produced the weight loss not exceeding 8% but in the paper [33] the Δm as high as 12% is described (Fig. 1).

In the third step of thermal changes of aerogel (till the temperature 1000°C) we found as typical the slow and progressive loss of water arising from OH-groups without any effect on the DTA curve. But on the TG curve slow and continual weight loss can be observed even in the temperature range from 800 to 1000°C.

In the case of our SiO_2–aerogel samples the total weight loss (20 to 1000°C) was between 12 and 15% but the weight loss 18% was also described [33].

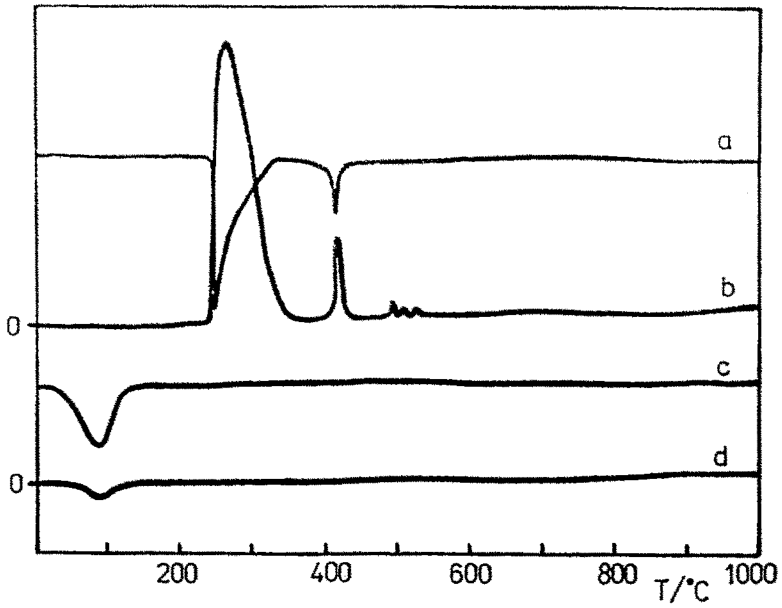

Fig. 1 DTG (a) and DTA (b) curves of the hydrophobic aerogel (fraction 0.4–0.75 mm), and DTG (c) and DTA (d) curves of the same aerogel annealed at 400°C

Conclusions

The results from thermal measurements of different SiO_2–aerogels samples published till now in comparison with our results show that SiO_2–aerogels prepared from tetramethoxysilane are thermally stable at least to the temperature 500°C and in such way some uses at elevated temperatures are possible (e.g. catalysts, catalyst carriers).

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