

## **CALCINATION OF SiO<sub>2</sub>-AEROGEL IN INERT ATMOSPHERE**

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### **Abstract**

Thermal treatment of SiO<sub>2</sub>-aerogel in inert atmosphere, in contrary to oxidizing atmosphere, yields a series of gas products with great range of mole masses (12–154 g mol<sup>-1</sup>) and every product has specific way of evolving. These substances are represented by CO, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and aromates. Part of evolving products, which are formed during catalytic condensation, is trapped under the surface and after carbonisation it causes opacity of surface layer of aerogel.

**Keywords:** gas products, SiO<sub>2</sub>-aerogel, thermal decomposition

### **Introduction**

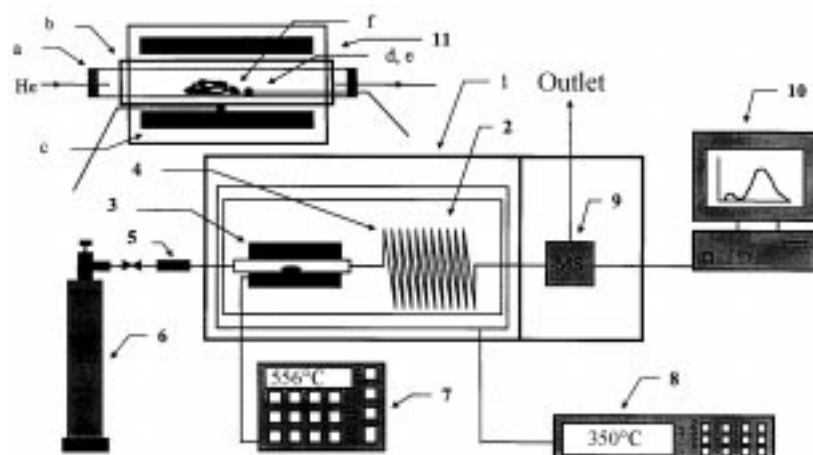
Calcination of aerogel in oxidizing atmosphere belongs to common procedures used for the preparation of transparent and hydrophilic samples of SiO<sub>2</sub>-aerogel. It can be assumed that the organic matter, which represents remains of solvent (methanol) and methoxy groups bound to SiO<sub>2</sub> skeleton, decomposes with the different mechanism of that in inert atmosphere. Calcination of SiO<sub>2</sub>-aerogel in inert atmosphere could yield a new type of sorbent. For some applications such a non-transparent aerogel could be very useful. Non-transparent SiO<sub>2</sub>-aerogel is usually prepared by adding carbon black to transparent aerogel with aim to increase absorbance in wavelength region below 8 μm and herewith to increase its thermo-insulating properties [1, 2].

The aim of this paper is to identify main decomposition products of hydrophobic SiO<sub>2</sub>-aerogel in inert atmosphere during programmed heating.

### **Experimental**

SiO<sub>2</sub>-aerogel was prepared from tetramethoxysilane (TMOS) which was hydrolysed by water solution of ammonia. The molar ratio of TMOS:H<sub>2</sub>O:NH<sub>4</sub>OH was 4:1:0.01. The preparation of SiO<sub>2</sub>-aerogel and its physico-chemical properties are described in detail in [3–5].

To remove air from the pores of aerogel prior to thermal decomposition, the sample of aerogel was several times evacuated and then flushed with helium at room temperature. After the removal of air the sample was heated in a silica tube (diameter 3 mm) placed in a small furnace. The sample was continually flushed by high grade purity helium which then passed through a restrictor and the products of thermal decomposition were registered by mass selective detector (HP 5971 A, Hewlett Packard, USA) and products were continually analysed during the experiment. Spectra were analysed by the commercial software and database 'NIST 98' for identification of samples analysed by the gas chromatography. Block diagram of the furnace and analytical apparatus used is shown in Fig. 1. Details about this apparatus were published in [6].



**Fig. 1** A block diagram of apparatus used for analysis of evolved gases. 1 – gas chromatograph; 2 – heated room; 3 – furnace with sample; 4 – capillary column; 5 – flow meter; 6 – pressure cylinder with carrier gas; 7 – temperature control unit; 8 – control unit of chromatograph; 9 – mass detector; 10 – personal computer; 11 – furnace in detail (a – inner silica tube, b – outer metal tube, c – heating body, d and e – regulating and indicating thermocouples, f – sample)

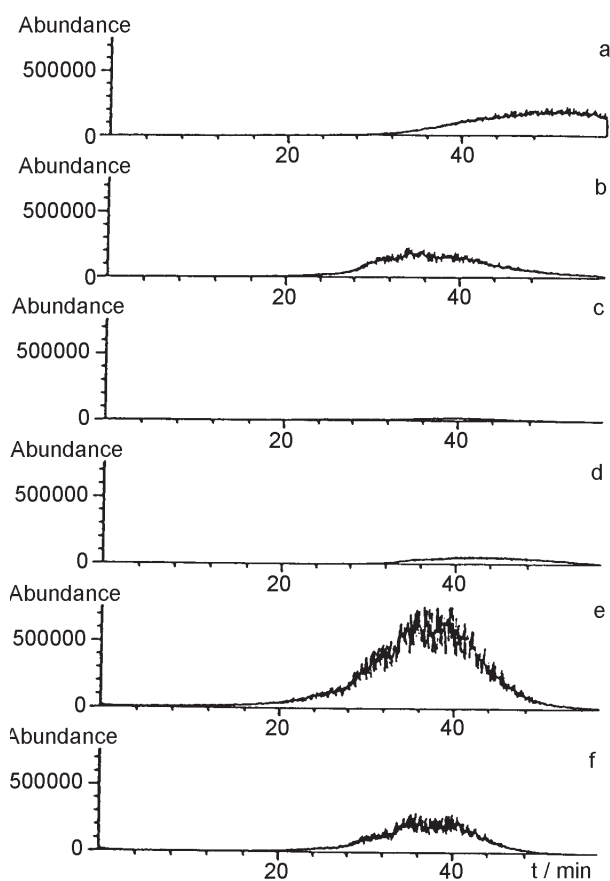
### Measurement conditions

The measurement conditions were the following: mass of sample: 30 mg, heating rate: 14°C min<sup>-1</sup>, carrier gas: He (purity: 99.99%, pressure: 130 kPa), temperature of MS detector: 250°C, frequency of recording spectra in SCAN mode: 0.2 Hz, region of  $m/z$ : 10–750 amu.

## Results and discussion

By the mass selective analysis about 90 different ions with relative mass ( $M/Z$ ) from 12 to 154 g mol<sup>-1</sup> can be identified during the heating of SiO<sub>2</sub>-aerogel in helium atmosphere. The amount of detected species is strongly effected by the temperature.

The water is one of the identified substances (Fig. 2c). The part of this water is formed during oxidation of organic matter by residual air in aerogel pores. The presence of CO<sub>2</sub> in decomposition products is evidence of this residual oxygen. The main part of water must be formed from hydroxyl groups bound to SiO<sub>2</sub> skeleton because it is released mainly over 600°C.

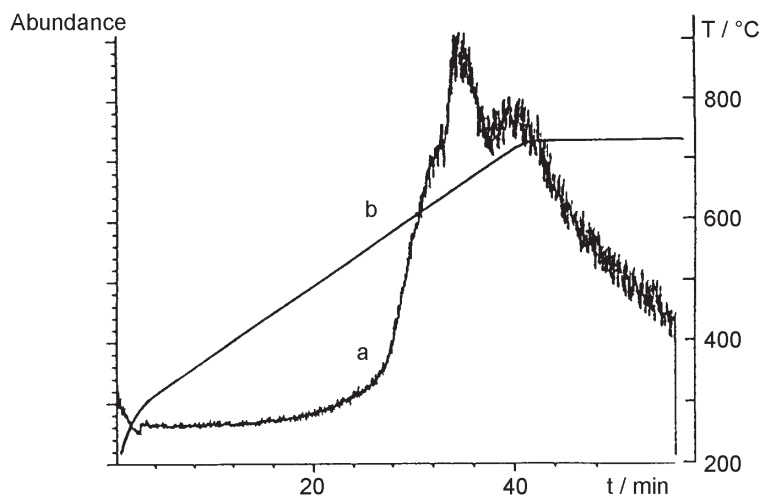


**Fig. 2** Release of a – CO, b – methane, c – H<sub>2</sub>O, d – ethane [ethene], e – formaldehyde and f – methanol during the heating of SiO<sub>2</sub>-aerogel in helium atmosphere. Plot of temperature vs. time is in Fig. 3

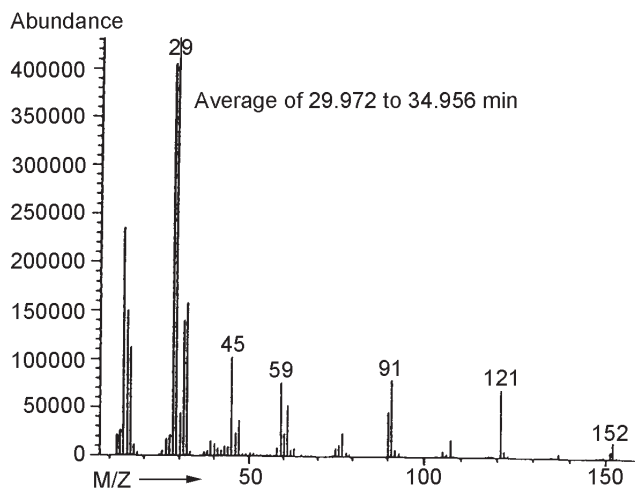
The release of formaldehyde starts at 400°C (Fig. 2c) and over the temperature of 500°C methane, ethane (ethene) (Figs 2b and d) and methanol are released (Fig. 2f). Because of the high temperature of this release it can be assumed that methanol is a product of synthesis and not a residual alcohol after supercritical drying.

There are two distinguished maxima at 670 and 720°C on the plot of sum of detected ions vs. temperature (Fig. 3). This means that the main process of the decomposition is shifted to higher temperature (by about 300°C) in comparison with decom-

position in oxidizing atmosphere [4]. From the time dependence of ion release it was found that the first peak is formed by ions with relative masses from 44 to 152 (44, 45, 46, 47, 59, 61, 77, 90, 91, 107, 121 and 152) and the second peak is formed by ions with relative masses 12, 13, 17, 26, 27, 30, 31 and 39. Some of these products can be identified as Co, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and aromates. The variety of decomposition products released in the first decomposition step (the first peak in Fig. 3) can be seen in the mass spectrum in Fig. 4. It can be assumed that at the first step smaller molecules are formed during the destruction of surface organic layer.



**Fig. 3** Sum frequency of detected ions releasing during dynamic heating in a – helium atmosphere and b – plot of temperature vs. time



**Fig. 4** The mass spectrum of ions releasing during dynamic heating in helium atmosphere in temperature interval from 600 to 680°C

Larger molecules are probably formed by catalytic effect of aerogel surface from small ones and then diffuse from aerogel and again partly decompose. A part of decomposition products diffuses from porous structure of aerogel and the other part remains decomposed in the form of carbon on the surface of the aerogel and causes the opacity of the sample. The end product of the calcination is non-transparent SiO<sub>2</sub>-aerogel. According to the high content of CO in the decomposition products (Fig. 2a) it can be also assumed that even over the temperature 700°C incomplete oxidation of organic molecules can occur.

## Conclusions

Calcination of SiO<sub>2</sub>-aerogel carried out in inert atmosphere is a complex process during which a great variety of gas products are evolved, mainly CO, CO<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and aromates. Physico-chemical properties of calcined aerogel, depending on residual organic film on the surface of aerogel frame, can be modified to a great extent by conditions of its thermal treatment. These conditions should be optimised for different practical applications in the future.

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