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Enhanced flame retardancy of hydrophobic silica aerogels by using sodium silicate as precursor and phosphoric acid as catalyst

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ABSTRACT

Organic groups on silica aerogels (SAs) introduced by surface modification not only achieve the hydrophobicity but also constitute the primary combustible components. In this study, the flammability of the typical precursor, i.e., tetraethoxysilane (TEOS) and sodium silicate (SS), synthetic SAs was investigated separately by cone calorimeter. The results demonstrated that SS based SAs had less fire hazards, smoke toxicity and larger critical heat flux, corresponding to lower flammability, compared to TEOS based SAs. Further research indicated that the lower flammability of SS based SAs should be attributed to a less quantity of organic groups which was related to their microstructure, especially specific surface area. The phosphorous components in SAs introduced by phosphoric acid contributed to improving the flame retardancy as the indication of a reduced gross calorific value. Besides, TG-DSC analysis revealed that SS based SAs had higher thermal stability with an improved onset temperature and peak temperature for the organic groups' oxidation reactions. Thus, it can be concluded that using sodium silicate as precursor and introducing phosphorous compounds contributed to improving the flame retardancy of SAs.

1. Introduction

Silica aerogels (SAs) are nanoporous materials consisting of over 95% air and less than 5% skeletons, which possess plentiful fascinating properties, such as an extremely low density, an ultra-low thermal conductivity, a high specific surface area [1–3]. Since first prepared by Kistler in 1931 [4], SAs have been used in numerous fields, e.g., thermal insulation, energy storage and conservation, catalyst supports and aerospace applications [2,5–9].

Currently, the preparation method of SAs is usually a classical two-step acid-base catalyzed sol-gel process [10] with using organosiloxane as precursors, e.g., tetraethoxysilane (TEOS) [11–13] and methyltrimethoxysilane (MTMS) [14–17]. For pursuing the hydrophobicity, a large amount of hydrophobic organic groups (derived from silylating agents) are introduced on SAs by surface modification. Besides, the residual unreacted organic groups on precursors and some organic solvent also remain in the nanoporous network of gels, which can further transfer into SAs. These organic components just constitute a potential fire risk of SAs when encountering thermal radiation and other materials' propagating flame under fire conditions. However, except for a few scholars [18], the flammability of hydrophobic SAs has not been paid sufficient attentions to date. At present, SAs are primarily

used for thermal insulation because of the extremely low thermal conductivity and usually considered as incombustible materials. Due to the complicated fire load in the thermal insulation systems, neglecting the fire hazards of the used materials makes the situation more dangerous.

Since the introduced hydrophobic organic groups are inevitable for acquiring the hydrophobicity, two strategies, i.e., changing precursors and adding flame retardants, are accessible to decrease the flammability of SAs. For the former, inorganic silicon sources like sodium silicate used as precursors have been reported broadly [19–21]. For the later, the added flame retardants should be compatible with the synthesis process and without compromising the excellent properties of SAs. It is known that an acid is usually used during the preparation of SAs (for hydrolysis) and phosphorous containing compounds are used as flame retardants widely [22–26]. Considering that, it is proposed appropriately to use phosphoric acid as flame retardant for preparing SAs.

In this study, we primarily focused on reducing the flammability of hydrophobic SAs. For this purpose, the flammability of typical precursor based SAs, i.e., TEOS and sodium silicate, was studied respectively. For another, the commonly used acid in the sol-gel process was changed to phosphoric acid for improving the flame retardancy of SAs.

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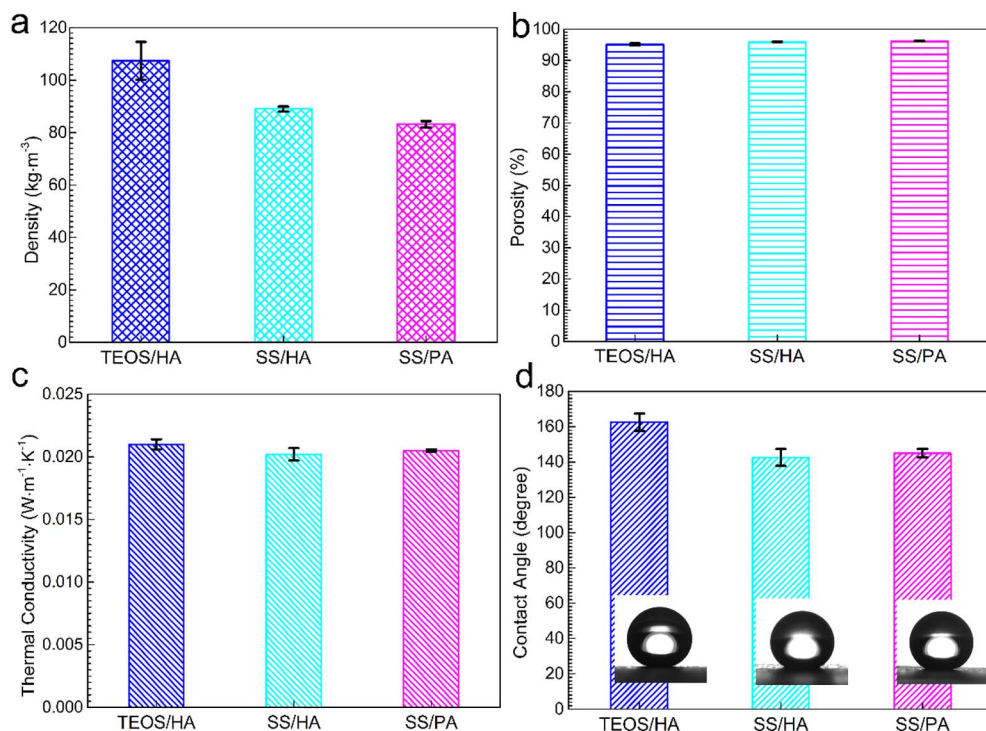


Fig. 1. Density (a), porosity (b), thermal conductivity (c) and contact angle (d) with the real photos as insets for the various SAs.

The effects of sodium silicate and phosphoric acid on lowering flammability were discussed in detail in our work.

2. Experimental

2.1. Raw materials

The typical precursors for the preparation of SAs were tetraethoxysilane (TEOS, Sinopharm Chemical Reagent Co., Ltd., SCRC, China) and sodium silicate (SS, 34%wt, modulus = 3.33, Qingdao Dongyue Sodium Silicate, Co., Ltd., China). Other chemicals including ethanol (EtOH), n-hexane, trimethylchlorosilane (TMCS), hydrochloric acid (36–38%), phosphoric acid (85%) and ammonium hydroxide (28%) were analytically pure which were purchased from SCRC and used as received.

2.2. Sample preparation

TEOS, EtOH, 0.1 M hydrochloric acid (HA) and 0.5 M ammonium hydroxide were used as precursor, solvent, acid and base catalyst respectively to synthesize alcolgel through a classical two-step acid-base catalyzed sol-gel process [27,28]. After aging with EtOH for 12 h, solvent exchange with n-hexane for 12 h, surface modification with 10% TMCS/n-hexane for 12 h, the SAs (denotes as TEOS/HA) were obtained finally through ambient pressure drying at 80 °C and 100 °C for 3 h, respectively.

For the preparation of SS based SAs, a single-step sol-gel process was adopted [29]. First the original SS was three times diluted with deionized water and gradually added into 2 mL hydrochloric acid or phosphoric acid (PA) until the pH of the sol was about 4.5–6.0. Then the sol was made air-tight and the gelation generally happened in 20 min. The obtained hydrogels were immersed with enough deionized water in a 250 mL beaker at 45 °C water bath for 10 h to remove the sodion [29]. The same procedures as TEOS/HA including aging, solvent exchange, surface modification and ambient pressure drying were performed subsequently to obtain SS based SAs, in which SAs corresponding to HA and PA were denoted as SS/HA and SS/PA, respectively. All the synthesis parameters were optimized.

2.3. Methods for characterization

The density (ρ) of SA powders was measured using a tap density meter. The porosity was calculated as follow.

$$\text{Porosity} = \left(1 - \frac{\rho}{\rho_s}\right) \times 100\% \quad (1)$$

where ρ_s is the skeletal density of SAs, usually $2200 \text{ kg}\cdot\text{m}^{-3}$. The thermal insulation of the specimens was estimated upon the thermal conductivity, using a thermal constants analyzer (TC3000E, XIATECH, China) at 25 °C in a vacuum container by transient hot wire method. The hydrophobicity of the specimens was characterized by contact angle measurement (CA, SL200K, KINO) by putting a water drop of 5 μL on the surface of SA powders.

The microstructures of the specimens were observed using a field emission scanning electron microscope (SEM, SIRION200, FEI). Furthermore, the nanopore structures were studied by N_2 adsorption-desorption measured at 77 K using a Tristar II 3020M analyzer and the temperature of outgassing was set to 200 °C. Specific surface area and average pore size were calculated using the Brunauer-Emmett-Teller (BET) method and the pore size distribution (PSD) and pore volume were calculated as per the Barrett-Joyner-Halenda (BJH) method. Fourier transform infrared spectra (FTIR, Nicolet 8700, TFS) were employed to study chemical bonds. The element content analysis was conducted by X Ray Fluorescence (XRF, XRF-1800). The thermal stability was carried out by TG-DSC analysis using a simultaneous thermal analyzer (Netzsch STA 449 F3) with a heating rate of 5 °C/min from ambient temperature to 800 °C in air atmosphere.

For studying the flammability of the prepared SAs, the corresponding tests were performed according to the ISO 5660 standard [30], using a cone calorimeter (Fire Testing Technology, UK) under the heat fluxes of 15, 25 and 35 $\text{kW}\cdot\text{m}^{-2}$. The specimens were the prepared SA powders of 200 mesh sieve, tiled uniformly in a tailored specimen holder of 80 mm \times 80 mm \times 10 mm. Each specimen was tested for three times with a typical reproducibility of $\pm 10\%$ for such tests [31] and the averages were reported in this work. The gross calorific value was tested using an oxygen bomb calorimeter (IKAC2000, Germany) as

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