Microporous and Mesoporous Materials 251 (2017) 105–113

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

The impact of Si/Al ratio on properties of aluminosilicate aerogels

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ARTICLE INFO

Article history:
Received 29 September 2016
Received in revised form
15 May 2017
Accepted 29 May 2017
Available online 2 June 2017

Keywords:
Aluminosilicate
Aerogels
Si/Al ratio
Sol-gel method
Supercritical drying

ABSTRACT

The Si/Al ratio is a key parameter of acid-base, structural, textural and, consequently, catalytic properties of amorphous crystalline (micro- and mesoporous) aluminosilicates. The changes of structural and textural characteristics of Al-Si aerogels with gradual increase of aluminum content are investigated. Aerogels were prepared via sol-gel method using prehydrolysed tetraethoxysilane and aluminium isopropoxide stabilized by acetylacetone. The gelation of the obtained sols took place in the presence of ammonia with the following drying in supercritical isopropanol. It was shown all aluminum reacts with prehydrolyzed tetraethoxysilane forming spherical particles in case the content of Al in the samples is less than 20 mol %. Aluminum drives the increase of interparticle coupling leading to the particle agglomeration, which is associated with the increase of the particle size and decrease of specific surface area and pore volume. For the samples with the aluminum content of >50 mol % the formation of pseudoboehmite plate-like particles is observed. The pseudoboehmite particles prevent the sintering of SiO_2 particles that leads to the increase of the aerogel specific surface area and pore volume. In case the high aluminum content (>80 mol %) the silica particles serve as a connector between boehmite plates. The ratio between Brønsted and Lewis acid sites decreases gradually with the increase of aluminum content of the aluminosilicate aerogels.

1. Introduction

The aerogels are the unique materials with low density, high porosity and specific surface area. Aerogels can be prepared from any oxides and their mixtures [1]. At the moment the SiO_2-based aerogels are well-studied materials. The synthesis routes and properties of silica aerogels, as well as the area of their potential applications can be found in many reviews [2–4] and original papers [5]. However, commercial use of SiO_2 aerogels is mostly limited to the heat insulation systems [6] and in Cherenkov detectors [7,8]. The multicomponent aerogels have wider range of applications. In particular the introduction of aluminum leads to the mixed aluminosilicate aerogels demonstrating a high potential as high temperature insulators [9], sorbents [10], glass and ceramics components [11,12], catalysts and their supports [13–15].

Tetraethoxysilane (TEOS) [16,17], partially prehydrolyzed TEOS [18–20] are often used as a Si precursor for Al − Si xerogel and aerogel synthesis. As an Al precursor the aluminum salts, such as nitrate [21], chloride [9], acetate [21], alkoxide [20,21], boehmite sol [22] are usually used. The main problem for the synthesis of aluminosilicate aerogel is the different hydrolysis rates of aluminum and silicon precursors. The inhibitors forming complexes with aluminum alkoxides such as acetylacetone [23] and ethyl acetoacetat [24] are used to slow down the hydrolysis of aluminum alkoxide.

Si/Al ratio is a key parameter that forms the acid-base, structural, textural and, for instance, catalytic properties of amorphous crystalline (micro- and mesoporous) aluminosilicates [25–29]. Hernandez and Pierre synthesized a series of aerogels with Si/Al varied from 0.25 to 20 using sol-gel method in acidic conditions (pH = 2) followed by drying in the supercritical CO_2. It has been shown that the Si/Al ratio affects the acidic properties, aluminum coordination and specific surface area [20]. Aravind and co-authors have prepared a series of Al-Si aerogels with Al_2O_3 content varied from 5 to 25 wt% using TEOS and boehmite sol via hydrolysis and saturation by helium in acid environment. The increase of Al content improves the thermal stability of aerogels [22]. However the

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http://dx.doi.org/10.1016/j.micromeso.2017.05.053
1387-1811/

systematic study of the impact of Si/Al ratio on properties of aluminosilicate aerogels have not been done till now.

This paper reports the evolution of the structure and properties (porosity, specific surface area, phase homogeneity, particle and cluster sizes and morphology, acidity) of Al-Si aerogels with a gradual increase of aluminum content. The series of Al-Si aerogels with different Si/Al ratios were synthesized via sol-gel method, using ammonia solution for gelation of Al-Si sol. The Al-Si gels were dried in supercritical isopropanol. The aerogels obtained have been investigated by ^{27}Al and ^{29}Si MAS NMR, FTIR CO adsorption, transmission electronic microscopy, X-ray diffraction, helium pycnometry and nitrogen adsorption methods to elucidate the characteristics of the synthesized materials.

2. Experimental part

2.1. Materials

Tetraethoxysilane (TEOS) + 98% by Acros Organics, aluminum isopropoxide (AliPrO) 98+% by Acros Organics, redistilled acetylacetone (acac) by the company «Vekton», isopropanol (iPrOH) by "NPO Himsintez" LLC, hydrochloric acid solution (HCl 32% aq., Sigma–Aldrich), ammonium hydroxide solution (NH_4OH 25% aq., Sigma–Aldrich) were used in the work.

2.2. Synthesis of Al-Si aerogels

The synthesis can be divided into two stages: preliminary hydrolysis of Si, Al precursors in an acid medium and gelation of Al-Si sol in alkaline medium of ammonia. Al–Si gels were prepared according to the scheme shown in Fig. 1. For the Al-Si gel synthesis prehydrolyzed TEOS ($H_2O/Si = 1.5$ $C_{Si} = 2.42$ mol/l) and solution AliPrO with acac (Al/acac = 2, $C_{Al} = 1$ mol/l) in isopropanol (iPrOH) were used. Prehydrolyzed TEOS was prepared by mixing TEOS 40 ml and iPrOH 29.16 ml with aqueous solution of HCl (4.84 ml) with pH = 2 (prepared by dissolving 0.1 ml of HCl 32 w.% aq. in 90 ml of distilled water). Before use it was kept at room temperature for more than two days. AliPrO/acac solution was prepared by mixing freshly distilled AliPrO (50 g) with iPrOH (184 ml); afterwards the acac (12.5 ml) was slowly added into the solution permanently stirring. Ammonia solution ($C_{NH3} = 3$ mol/l) was prepared by diluting an aqueous solution of ammonia (11.25 ml) in 50 ml of iPrOH.

The AliPrO/acac solution was added to the previously hydrolyzed TEOS while stirring. Volume of solutions used to prepare a series of gels is shown in Table S1, according to the necessary concentration of aluminum. Afterwards the solution obtained was boiled at reflux for 30 min. Next, an aqueous solution of HCl with pH = 2 in amount equal to the number of moles of aluminum ($H_2O/Al = 1$) with 1 ml of iPrOH was added and boiled for another 30 min. Since the aluminum concentration in the AliPrO/acac solution is lower than in the synthesized sol, after the step of boiling the excess of iPrOH was taken away by distillation to get aluminum content of 50, 80, 90, 100 mol % in finished gel (shown in Table S1). The Al-Si sol was cooled and poured out into a plastic container resulting in the sol formation. Then, distilled water, ammonia solution and iPrOH mixture was added into Al-Si sol. Final the volume of the samples was 20 ml with total concentration of Si and Al equal to 1,33 mol/l. The water amount for gel synthesis was equal to the stoichiometric value to obtain the corresponding hydroxides, taking into account the water in the ammonia solution. Water was added according to the equation: $n_{H2O} = (n_{Si}*4+n_{Al}*3) * 1.15$. Ammonia was added according to the equation: $n_{NH3} = n_{Si}/3 + n_{Al}/1.6$.

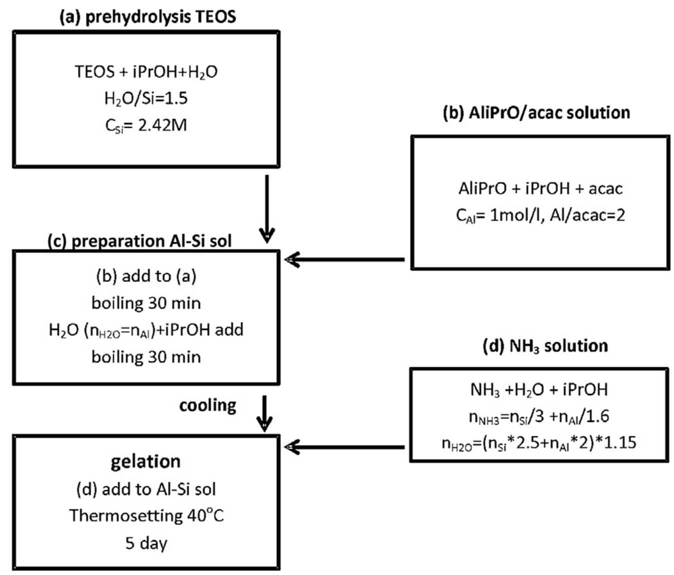

Fig. 1. Schematic synthesis of Al-Si gels.

For gelation and gel syneresis, the hermetically closed container was placed in the thermostat (at 40 °C). The containers with gel were kept in thermostat for 5 days. During washing the gels from hydrolysis products by iPrOH, the solvent was changed every 12 h in the course of these 5 days. The gel was dried in the supercritical isopropanol, for which the gel was placed into 300 ml autoclave and flooded with 150 ml iPrOH containing 3 vol % of water. Afterwards the pressure was increased up to 50 atm by argon and heated up to 300 °C at a rate of 90 °C/h. The pressure in the autoclave was maintained at 100 atm until the desired temperature was reached. Then the pressure was released at a rate of 0.4 atm/min to ambient pressure, after which autoclave was cooled.

A series of aerogels with aluminum content varying from 2 to 90 mol % was prepared, the Si/Al ratio varied from 49 to 0.11. In addition to Al-Si aerogels, a sample of alumina aerogel was prepared for the comparison using the similar procedure. Table 1 shows the sample names, the aluminum content, Si/Al ratio, and gelation time. Gelation time of sols was ranged from few hours to few minutes, depending on the aluminum content. Sol with aluminum content <50 mol % solidifies during the gelation into a solid gel. Consolidation of the solid gel occurs during in daytime then the gel can be easily removed from the vessel. During the gelation the sol with more than 50 mol % of aluminum transforms into a viscous liquid followed by a slow solidification and then compaction. This is the reason to keep the gels in thermostat at 40 °C for 5 days.

2.3. Physical methods

Textural characteristics of the samples were determined via low-temperature nitrogen adsorption isotherms using ASAP-2400 setup (Micromeritics, United States). The specific surface area was calculated by BET, the pore size distribution was determined by BJH.

Porosity was calculated by equation $\phi = (1-\rho_{bulk}/\rho_{particle}) * 100\%$, where ρ_{bulk} is apparent density of material (the ratio of material mass to the sum of pore volume and solid phase), $\rho_{particle}$ is real material density, ρ_{bulk} is the ratio of the sample mass of aerogel to its volume, measured by the equation l*m*n, where l, m, n are the length, width and height of aerogel block, respectively. $\rho_{particle}$ was measured by AutoPycnometer 1320 (Micromeritics, United States).