

# Infrared spectroscopic study of octahydrodoctasilsesquioxane hydrolytic polycondensation<sup>☆</sup>

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## ARTICLE INFO

### Article history:

Available online 4 June 2014

### Keywords:

Mesoporous silica  
Amorphous silica  
Hydrolytic polycondensation  
Octahydrodoctasilsesquioxane

## ABSTRACT

Spectroscopic studies are very important to characterize the structure of amorphous mesoporous silica. In this study, mesoporous silica was obtained by hydrolytic polycondensation of octahydrodoctasilsesquioxane and tetraethoxysilane. Infrared spectra of the reaction products and commercially available different forms of amorphous silica were measured. Spectra were analyzed directly and after the decomposition process using a band fitting procedure. In a hydrolytic polycondensation process both, alkoxy groups in tetraethoxysilane and hydrogen atoms in octahydrodoctasilsesquioxane are transformed to reactive Si—OH groups which can subsequently condense forming Si—O—Si bridges. However, as evidenced, not all Si—OH groups react. The main bands in the spectra of the obtained xerogels are due to the vibrations of SiO<sub>4</sub> group:  $\nu_{as}$ Si—O—Si,  $\nu_s$ Si—O—Si and  $\delta$ O—Si—O. The bands due to Si—H and Si—OH vibrations are also observed.

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## 1. Introduction

Silsesquioxanes are very important and fascinating compounds which have gained an increased attention in recent years because of their applicational properties. Among them, spherosilsesquioxanes are the most interesting compounds due to their specific “architecture” [1]. Completely inorganic octahydrodoctasilsesquioxane – T<sub>8</sub><sup>H</sup>, which possesses only a hydrogen atom as the substituent at each silicon atom [2,3] has focused our attention. Its low dielectric constant and other superior insulating properties are expected to be transferred to the new material obtained from octahydrodoctasilsesquioxane. As has been shown recently, hydrolytic polycondensation process of T<sub>8</sub><sup>H</sup> molecules leads to amorphous and mesoporous silica of unique structure [4,5].

Outstanding applicability (e.g. in catalysis [6], sorption processes [7], medicine [8]) of mesoporous silica has attracted the attention of scientists for the past 20 years. Mesoporous silica of different porous and morphological characteristics has been synthesized [9–15] for the last thirty years. Importance of this material is reflected in a steady research in this field. Most often

mesoporous silica has been obtained using organic template molecules or surfactants as structure directing agents. However, a surfactant- and template-free approach has also been utilized and described [16].

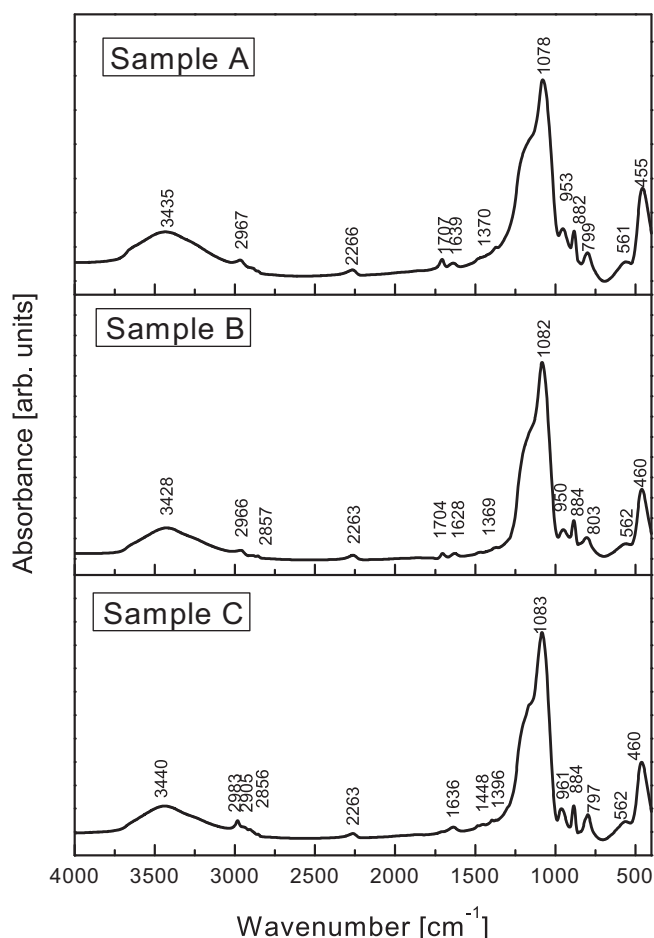
In the work presented here, T<sub>8</sub><sup>H</sup> and TEOS-derived mesoporous silica was obtained without any structure directing agents (surfactant or template). The synthesized material has extremely fine surface properties (BET surface area of approximately 800 m<sup>2</sup>/g and almost no micropore population). T<sub>8</sub><sup>H</sup> was used as the main precursor of silica, and tetraethoxysilane was added to the reaction as the co-monomer. An assumption was made that the molecules of TEOS would act as a bridge between the T<sub>8</sub><sup>H</sup> cages. However, TEOS molecules can also condense with each other and form more complex molecules of different sizes. Therefore addition of TEOS increases pore volumes.

XRD investigations revealed that the obtained mesoporous silica was amorphous, thus we compared these samples with other amorphous silicon dioxides, i.e. vitreous SiO<sub>2</sub>, aerosil and silica gel. Common feature of all amorphous silica is the presence of [SiO<sub>4</sub>] tetrahedron as the structural basic unit [17]. Amorphous substances are characterized by a lack of long-range order; therefore spectral bands are broad and of complex shape. Vibrational spectroscopy in the mid-infrared spectral range is an excellent method to characterize vibrations of the SiO<sub>4</sub> units as it has been done in the past [18,19]. Moreover, it is the most important method for structural studies of amorphous materials. In the mid-infrared region, the bands due to fundamental vibrations of [SiO<sub>4</sub>] tetrahedron in

<sup>☆</sup> Selected paper presented at XIIth International Conference on Molecular spectroscopy, Krakow – Bialka Tatrzańska, Poland, September 8–12, 2013.

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**Fig. 1.** MIR spectra of mesoporous silica obtained: from 0.5 g  $T_8^H$  – Sample A, from 0.25 g  $T_8^H$  – Sample B, from  $T_8^H$  and TEOS in the ratio (SiH):(OC<sub>2</sub>H<sub>5</sub>) = 1:1 – Sample C.

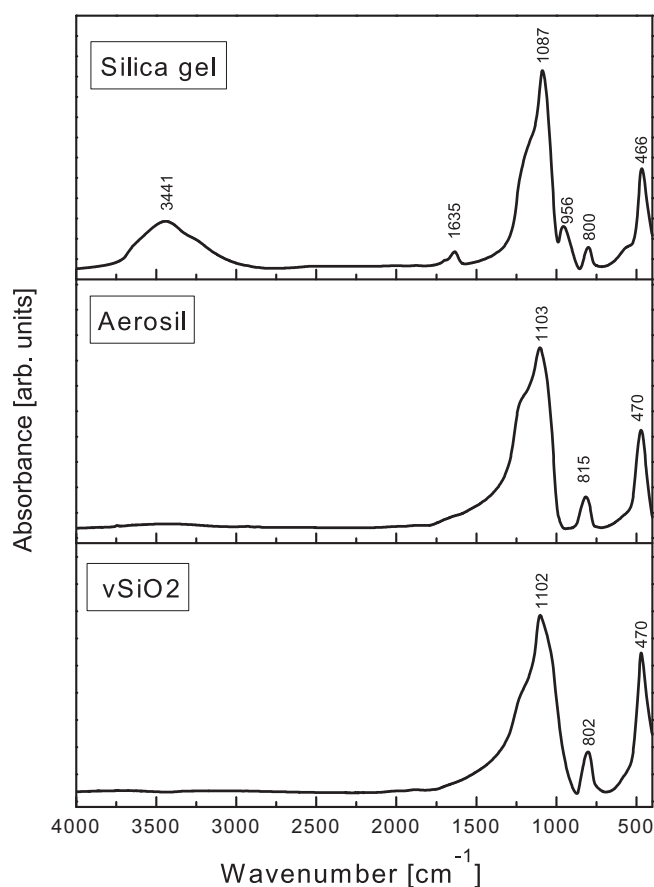
the SiO<sub>2</sub> framework are observed [20,21]. There is extensive literature concerning spectroscopic studies of the sol–gel silica materials [22–24].

The aim of this study was to characterize the products of hydrolytic polycondensation of  $T_8^H$  and TEOS. A detailed analysis of vibrational spectra of the obtained materials was carried out. Comparison of the measured spectra with the spectra of commercially available forms of silica (silica gel, aerosil, silica glass) provides important information on the structure of the obtained materials. This approach has allowed us to make precise band assignments to appropriate vibrations.

## 2. Experimental

### 2.1. Preparation of xerogels

Mesoporous silica was obtained by hydrolytic polycondensation of octahydrodoctasilsesquioxane with the addition of tetraethoxysilane. The process was catalyzed by tetra-*n*-butylammonium hydroxide. All chemicals were used as supplied: octahydrodoctasilsesquioxane from Hybrid Plastics Inc., TEOS from Sigma–Aldrich®, tetrahydrofuran from Chempur and TBAH – tetra-*n*-butylammonium hydroxide (1.0 mol/L solution in methanol) from Alfa Aesar. Hydrolysis was carried out in argon atmosphere in a three-neck flask at room temperature. The ratio between Si–H groups in the  $T_8^H$  molecules and ethoxy groups from TEOS was 1:1. A more detailed description of the preparation procedures can be found elsewhere [5].



**Fig. 2.** MIR spectra of silica gel, aerosil and  $vSiO_2$ .

Vitreous SiO<sub>2</sub> ( $vSiO_2$ ) was obtained by melting of high purity quartz. Silica gel and aerosil were purchased from LACH-NER and Sigma–Aldrich®, respectively.

### 2.2. Method of analysis

Mid-infrared spectra (4000–400  $cm^{-1}$ ) were measured on a Bruker Vertex 70V infrared spectrometer using 168 interferogram scans at 4  $cm^{-1}$  resolution. Samples were prepared by the standard KBr pellet method using KBr supplied by Merck.

The resulting spectra were decomposed according to a method proposed and described by Handke et al. [18]. The calculations were carried out with commercially available SPECTRAL-CALC® program distributed by Galactic Industries Corporation.

## 3. Results and discussion

The structure of  $T_8^H$  and TEOS condensation products was examined by infrared spectroscopy. The spectra of the obtained materials and the spectra of well defined amorphous silica samples were compared (Figs. 1 and 2). Spectra of amorphous silica samples were measured in the range of 4000–400  $cm^{-1}$ . In this spectral region important similarities and differences in the sample composition and structure can be observed. Band positions in the spectra of silica samples obtained by hydrolytic polycondensation of  $T_8^H$  (Fig. 1 – samples A and B) and  $T_8^H$  + TEOS (Fig. 1 – sample C) are almost the same, but differences in band intensities are observed. The bands due to silicon-oxygen bond vibrations, in accordance with the SiO<sub>4</sub> tetrahedral symmetry, can be referred to four  $A_1$ , E and  $2F_2$  modes, which can be described as follows:

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