

## Organic groups influencing microporosity in organosilicas

A. Petra Dral, Johan E. ten Elshof\*

MESA + Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands



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### ABSTRACT

The micropore structure of a series of organosilica materials with various organic groups in bridging (methylene, ethylene, hexylene, octylene, *p*-phenylene) and terminal (methyl, *n*-propyl) positions was analyzed and compared to that of inorganic amorphous silica. Vapor thermogravimetry with water, methanol, 1-propanol and cyclohexane vapors was used to measure accessible pore volumes, pore entrance sizes and surface chemistries. Gas pycnometry with He, Ar and N<sub>2</sub> was used to measure skeletal densities, semi-quantitative surface-to-volume ratios and surface areas, pore entrance sizes and semi-quantitative pore cavity sizes. Conventional adsorption isotherms were measured for N<sub>2</sub> at –196 °C to check for mesoporosity and for CO<sub>2</sub> at 0 °C to obtain Brunauer-Emmett-Teller surface areas for comparison. The known classification of 1) short or rigid organic bridges that open up the pore structure, 2) longer and more flexible bridges that cause pore filling and 3) terminal organic groups that reduce pore formation is further specified. The incorporation of any organic group in the silica network increased the dispersity in micropore entrance sizes as compared to inorganic silica in the probed size range. A critical discussion is given of the commonly accepted ‘spacing concept’ of organic bridges.

### 1. Introduction

The incorporation of organic groups in amorphous silica networks, i.e. replacement of Si-O-Si linkages with Si-R or Si-R-Si linkages, influences various functional properties such as mechanical flexibility and fracture resistance [1,2], hydrophobicity [3–5] and hydrothermal stability [5–8]. For applications that make use of the microporosity of organosilica materials, such as separation membranes, varying the nature and location of the organic groups allows tuning of micropore sizes and surface chemistries. Organic groups in bridging position (Si-R-Si) are part of the network backbone and act as spacers when they are short or rigid such as methylene (-CH<sub>2</sub>-), ethylene (-C<sub>2</sub>H<sub>4</sub>-), ethenylene (-C<sub>2</sub>H<sub>2</sub>-) and phenylene (-C<sub>6</sub>H<sub>4</sub>-) groups [9–15]. Though methylene-bridged silica networks have only single-atom spacers between neighboring Si atoms, similar to inorganic silica, the network opens up because Si-C bonds (1.97 Å) are longer than Si-O bonds (1.57–1.59 Å) [16]. Si-C-Si bonds are also more rigid because they do not have the impressive freedom of over 40° variation in bond angle that Si-O-Si bonds have [17]. Long and flexible bridges such as hexylene (-C<sub>6</sub>H<sub>12</sub>-) and octylene (-C<sub>8</sub>H<sub>16</sub>-) groups tend to collapse and fill up the empty space [12,13,18–20]. The bulkiness of these bridges is still sufficiently low to allow high network condensation degrees [5], but they transform the network towards a flexible polymer-like structure through which molecules can pass based on affinity rather than through pre-existing pore channels [12,20]. Membrane permeation data have shown that the effective pore entrance size generally increases for bridges in the order

O (inorganic silica) < CH<sub>2</sub> < C<sub>2</sub>H<sub>4</sub> < C<sub>3</sub>H<sub>6</sub> < C<sub>6</sub>H<sub>12</sub> < C<sub>8</sub>H<sub>16</sub> and C<sub>2</sub>H<sub>4</sub> < *p*-C<sub>6</sub>H<sub>4</sub> < C<sub>8</sub>H<sub>16</sub> [9,12,20,21]. If organic groups are placed in terminal position (Si-R), they do not act as spacers between adjacent Si atoms and easily fill up the pores created by the silica backbone. However, terminal methyl (-CH<sub>3</sub>) and phenyl (-C<sub>6</sub>H<sub>5</sub>) groups have also been reported to increase the effective pore opening size in membrane applications as compared to inorganic silica [22] and methyl groups can increase the total pore volume [3]. Organic groups in terminal position increase the network hydrophobicity by sticking out at the pore surface [3,4,22,23].

Although the incorporation of short or rigid organic bridges between Si atoms clearly increases the size of part of the micropore entrances and/or cavities, this ‘spacing concept’ requires a closer look. Firstly, the effect of organic bridges acting as spacers between Si atoms tends to be generalized to the expansion of *all* micropores. However, it should be kept in mind that about 75% of the bridging units still remains the same (Si-O-Si) as in inorganic silica networks when using trialkoxysilyl precursors. The formation of small rings with only Si-O-Si linkages is still possible. Molecular dynamics simulation studies on inorganic and ethylene-bridged silica networks predict a reduction of the number of smallest pores but not their disappearance [11,24], though the random distribution of ethylene bridges in these models differs from reality. The generally observed superiority of inorganic silica membranes in terms of reaching the highest permeation selectivities for very small molecules such as H<sub>2</sub>O and H<sub>2</sub> is thus not self-evident.

Secondly, the pore size expansion in organically bridged networks

\* Corresponding author.

E-mail address: [j.e.tenelshof@utwente.nl](mailto:j.e.tenelshof@utwente.nl) (J.E. ten Elshof).

that is achieved in reality, does not only result from the bridges acting as spacers between Si atoms but also results from altered kinetics during network compaction in sol-gel processing. The incorporation of organic bridges changes the size, shape, flexibility and connectivity of the monomer unit. These properties affect the monomer mobility during drying and consolidation of the material after synthesis. For example, methylene- and ethylene-bridged silica monomers are about twice as large as inorganic silica monomers, have six connection points to the surrounding network instead of four and have a linear shape instead of spherical. This yields a lower monomer mobility during compaction, which in turn increases the number of pores that are kinetically trapped at larger sizes and also different shapes than preferred thermodynamically. Some experimental results on these effects can be found in a consolidation study previously reported by us [25]. Elaborate data sets of entire micropore structures in organosilica materials to further evaluate these issues are scarce. Commonly used membrane permeation measurements mainly probe the bottlenecks along permeation pathways and cryogenic adsorption ( $N_2$ , Ar) excludes the smallest micropores due to diffusion limitations.

In the present study, in-depth comparative data on the microporous networks of a range of organosilica materials is obtained via our recently reported method of vapor thermogravimetry (TG) and gas pycnometry (PM) [26]. This method uses a range of solvents and non-polar gases to probe micropore volumes, sizes and surfaces at room temperature. (Organo)silica materials were prepared from the precursors listed in Fig. 1 by sol-gel processing. The presence of mesoporosity was analyzed with conventional  $N_2$  adsorption isotherms at  $-196^\circ\text{C}$ . Vapor TG was used to measure accessible pore volumes, pore entrance sizes and surface chemistries. Gas PM was used to measure skeletal densities, semi-quantitative surface-to-volume ratios and surface areas, pore entrance sizes and semi-quantitative pore cavity sizes. Water, methanol, 1-propanol and cyclohexane were used as vapor probe molecules for TG. He, Ar and  $N_2$  were used as gas probe molecules for PM. The above discussed classification of 1) short or rigid organic bridges that open up the pore structure, 2) longer and more flexible bridges that cause pore filling and 3) terminal organic groups that reduce pore formation is used as framework for the discussion and is further specified. A relation between the incorporation of organic groups and the dispersity in pore entrance sizes is presented.

## 2. Experimental

### 2.1. Chemicals

Bis(triethoxysilyl)methane (97% purity), 1,2-bis(triethoxysilyl)ethane (97% purity), 1,6-bis(trimethoxysilyl)hexane (97% purity), 1,8-bis(triethoxysilyl)octane (97% purity), 1,4-bis(triethoxysilyl)benzene (95% purity), 1,2-bis(methyldiethoxysilyl)ethane (purity unknown), methyltrimethoxysilane (97% purity), *n*-propyltrimethoxysilane (98%

purity) and tetraethoxysilane (99% purity) were obtained from ABCR. Nitric acid was obtained from Sigma Aldrich (70 wt% aqueous solution) and Acros (65 wt% aqueous solution). Anhydrous ethanol (purity 99.8%,  $< 0.01\%$   $H_2O$ ) was obtained from VWR and SeccoSolv. Anhydrous methanol (purity 99.8%,  $< 0.005\%$   $H_2O$ ) was obtained from VWR. Anhydrous 1-propanol (purity 99.9%) and cyclohexane (purity  $> 99\%$ ) were obtained from Alfa Aesar.

### 2.2. Sample preparation

(Organo)silica materials were synthesized as reported elsewhere [5]. The  $HNO_3 : H_2O : \text{alkoxy}$  ratio was 0.064 : 1.1 : 1.0, as derived from Castricum et al. [12]. The resulting materials were ground to powder by ball milling and were consolidated at  $300^\circ\text{C}$  in  $N_2$  for 3 h. All samples were stored under ambient conditions.

### 2.3. Thermogravimetry

Thermogravimetric data was recorded as reported elsewhere [26]. In short, the sample was dried at  $200^\circ\text{C}$  in synthetic air ( $N_2:O_2$  80:20 vol:vol) for 4 h, stabilized at  $30^\circ\text{C}$  in synthetic air for 1 h, filled with vapor at  $30^\circ\text{C}$  in humidified  $N_2$  for 18 h, flushed at  $30^\circ\text{C}$  in synthetic air for 1 h and dried at  $200^\circ\text{C}$  in synthetic air for 4 h. The supplied gases were dried with SGE packed column moisture traps and the  $N_2$  was subsequently humidified by bubbling through a solvent at room temperature.

### 2.4. Pycnometry

Pycnometry measurements were done as reported elsewhere [26]. In short, the sample was loaded in the sample cell and dried in an oven at  $150^\circ\text{C}$  under  $N_2$  flow for 3 h. Immediately afterwards, the sample was weighed and loaded in the pycnometer. The apparent sample volume was analyzed with He, He + He, He +  $N_2$ , Ar,  $N_2$  and  $N_2 + N_2$  (measured in this order). The measurement series started with He because of its smallest size and lowest adsorption, which facilitates removal of atmospheric residues from the pores prior to data collection.

### 2.5. Adsorption isotherms

Adsorption isotherms were collected with a Quantachrome Instruments Autosorb-1 and the gases were led through a moisture trap before entering the set-up. The sample was outgassed at  $300^\circ\text{C}$  for 3 h. Adsorption isotherms were collected for  $CO_2$  at  $0^\circ\text{C}$  and for  $N_2$  at  $-196^\circ\text{C}$ . Brunauer-Emmett-Teller (BET) curves derived from  $CO_2$  adsorption were based on at least 4 data points.

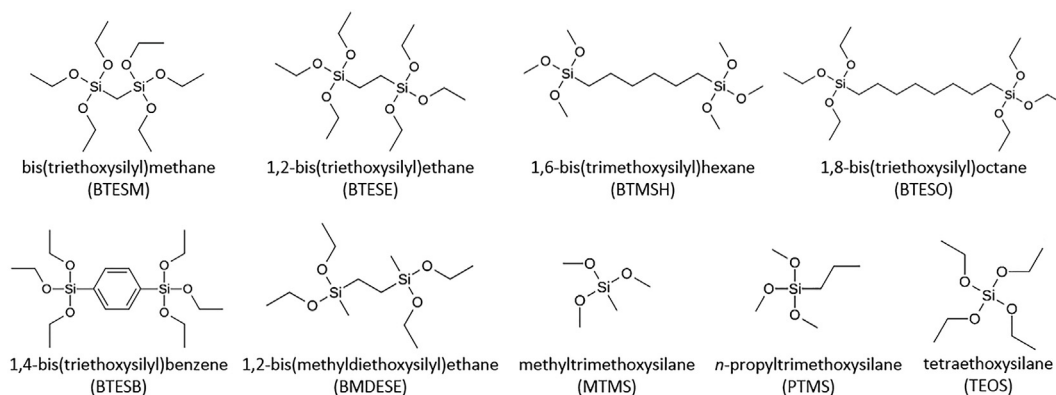


Fig. 1. Chemical structures and abbreviations of the used (organo)silica precursors.

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