

# Synthesis and characterization of hydrogen selective silica membranes prepared by chemical vapor deposition of vinyltriethoxysilane



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## ABSTRACT

Hydrogen-selective silica membranes were prepared on a macroporous alumina support by chemical vapor deposition (CVD) of vinyltriethoxysilane (VTES) at 873 K at atmospheric pressure. The membrane had a high H<sub>2</sub> permeance of  $5.4 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  with H<sub>2</sub> selectivity over CO<sub>2</sub>, N<sub>2</sub>, CO and CH<sub>4</sub> of 95, 170, 170 and 480, respectively. In situ Fourier transform infrared (FTIR) measurements after CVD on an alumina disk at the same conditions as for the membrane preparation showed that the vinyl groups remained in the silica structure. The VTES-derived membrane had higher hydrothermal stability than a pure tetraethoxyorthosilicate (TEOS)-derived silica membrane, during exposure to 16 mol% water vapor at 872 K for 72 h. The temperature dependence of the permeance of various molecules (He, Ne, H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CO, CH<sub>4</sub>) before and after hydrothermal treatment gave information about the mechanism of permeance and the structure of the membrane. The membrane was composed of a contiguous silica network through which small species permeated by a solid-state mechanism and a small number of pores through which the large molecules diffused. The silica-based structure became more compact after hydrothermal treatment with decreasing permeance of small molecules (He, Ne, H<sub>2</sub>), while small pores were enlarged increasing permeance of large molecules (CO<sub>2</sub>, N<sub>2</sub>, CO, CH<sub>4</sub>). Calculation results for the small species based on a mechanism involving jumps of the permeating species between solubility sites showed lower activation energy and larger jump distances than those of a TEOS-derived silica membrane. The retention of the vinyl groups in the structure mostly associated with the defect pores resulted in interactions with CH<sub>4</sub> and CO<sub>2</sub>, so that these species permeated by a surface diffusion mechanism.

## 1. Introduction

Gas separation membrane technology has been receiving increasing attention because of its inherent advantages in energy-efficiency, cost-effectiveness and environmental compatibility over other methods like distillation or pressure swing adsorption [1,2]. Polymeric membranes have been widely used as gas separation membranes, but suffer from low permeance and selectivity and are not resistant at severe working conditions. Although palladium-based metal composite membranes have high hydrogen permeance and selectivity, they also have low chemical resistance and high cost. On the other hand, inorganic silica-based membranes are promising materials for various kinds of gas separations due to their excellent gas separation properties coupled with high chemical resistance and thermal stability, as well as moderate cost [3–7]. Since the first reports of silica-based membranes by Okubo and Inoue [8] and the group of Gavallas [9], tetraethylorthosilicate (TEOS)-derived silica-based membranes have been intensely studied and

synthesis by sol-gel methods [10–13] and chemical vapor deposition (CVD) methods [14–17] have been reported. From previous studies TEOS-derived membranes are comprised of a silica network with isolated solubility sites of about 0.3 nm that allow only small molecules such as helium (0.260 nm), neon (0.275 nm) and hydrogen (0.289 nm) to permeate by a solid-state hopping mechanism, resulting in high hydrogen selectivity over large molecules such as nitrogen (0.364 nm) and methane (0.380 nm) [18,19]. For that reason TEOS-derived membranes have been used in various applications, such as methane-steam reforming, where hydrogen separation is important [20,21]. However, the small size of the openings and the low hydrothermal stability of TEOS-derived pure silica membranes have limited the widespread applications of the membranes, and hence development of a controllable silica network size and improvement of hydrothermal stability are highly desirable [22,23]. Precursors in which the siloxanes are substituted with large pendant groups give rise to a connected pore structure and enhanced permeance in certain cases [24]. In addition,

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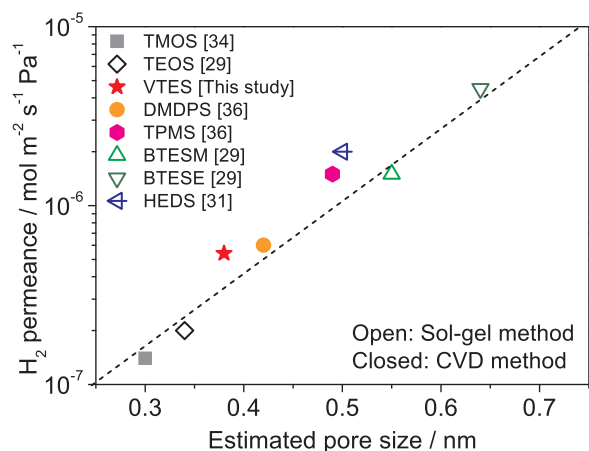


Fig. 1. Comparison of H<sub>2</sub> permeance for various silica membranes as a function of their estimated pore size.

the organic moieties can improve hydrothermal stability because of their -hydrophobicity [25–27].

Although H<sub>2</sub>-selective, pure silica membranes prepared by CVD consist of a continuous silicious network with pores only present as defects, it is possible to design materials with pores useful for the separation of larger gaseous molecules. Raman and Brinker first proposed a method to control the pore size of microporous silica membranes by using templates in the sol-gel method [28], and since then there have been a number of reports on the tuning of the network size of silica membranes by using various silica precursors via both the sol-gel and CVD methods. Fig. 1 shows the H<sub>2</sub> permeance of silica membranes derived from different silica precursors as a function of their estimated pore size. The H<sub>2</sub> permeance increase with increasing estimated pore size, but as expected, H<sub>2</sub> selectivities over large molecules such as CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> decrease with increasing pore size. Kanazashi et al. prepared organic-inorganic hybrid silica membranes by the sol-gel method using bridged alkoxides such as bis(triethoxysilyl)methane (BTESM), bis(triethoxysilyl)ethane (BTESE) as silica precursors [29,30]. The pore size distribution determined by fitting to a normalized Knudsen-based permeance (NKP) suggested that the average pore size was in the following order: BTESE-derived silica (0.64 nm) > BTESM-derived silica (0.55 nm) > TEOS-derived silica (0.34 nm). It should be noted that the BTESM-derived membranes showed a high C<sub>3</sub>H<sub>6</sub> permeance of  $6.32 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  with a selectivity over C<sub>3</sub>H<sub>8</sub> of 8.8 at 323 K indicating reasonably good pore size control. Lee et al. prepared silica membranes by the sol-gel method using disiloxanealkoxides such as tetraethoxydimethyldisiloxane (TEDMDS) and hexaethoxydisiloxane (HEDS) [31,32]. The order of estimated pore size was TEDMDS-derived silica (0.70 nm) > HEDS-derived silica (0.50 nm) > TEOS-derived silica (0.32 nm). The TEDMDS-derived membrane had high H<sub>2</sub> permeance of the order of  $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , but low H<sub>2</sub>/N<sub>2</sub> selectivity below 20 indicating that transport occurred through the pores. Kusakabe et al. prepared silica membranes by the sol-gel method using mixtures of TEOS and pendant-type alkoxides with carbon chain substitution such as octyltriethoxysilane, dodecyltriethoxysilane (DTEOS) and octadecyl-triethoxysilane. The TEOS-DTEOS-derived membrane showed a higher pore size distribution than the TEOS-derived membrane of around 0.3–0.4 nm, which was estimated based on single gas permeation tests [33]. Nomura et al. prepared a silica membrane by the counter diffusion CVD method using tetramethoxysilane (TMOS) and O<sub>2</sub> [34]. The membrane had H<sub>2</sub> permeance of  $1.5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and H<sub>2</sub>/N<sub>2</sub> selectivity over 1000, and was stable under the typical steam-reforming conditions of methane (76 kPa of steam at 773 K) for 21 h. Nomura et al. also prepared silica membranes using various pendant type alkoxides such as methyltrimethoxysilane (MTMOS), trimethylmethoxysilane (TMMOS),

propyltrimethoxysilane (PrTMOS), phenyltrimethoxysilane (PhTMOS) [35]. The membranes prepared using methyl substituted precursors had H<sub>2</sub> permeance of  $0.6\text{--}1.4 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and H<sub>2</sub>/N<sub>2</sub> selectivity over 200 with estimated pore sizes of about 0.3 nm. The membranes prepared using larger functional groups (PrTMOS, PhTMOS) showed an order of magnitude higher H<sub>2</sub> permeance but smaller H<sub>2</sub>/N<sub>2</sub> selectivity below 40 with maximum pore sizes around 0.5 nm. Thus, the authors concluded that the pore size of the silica membranes can be controlled by changing the type of silica precursors. Nakao and collaborators prepared silica membranes by the counter-diffusion CVD method using methoxysilanes with different numbers of substituted phenyl groups such as phenyltrimethoxysilane (PTMS), dimethoxydiphenylsilane (DMDPS) and triphenylmethoxysilane (TPMS) at 873 K [36,37]. The order of estimated pore size based on the normalized Knudsen-based permeance was TPMS-derived silica (0.486 nm) > DMDPS-derived silica (0.42 nm) > PTMS-derived silica. The DMDPS and TPMS-derived membranes had high H<sub>2</sub> permeances of the order of  $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and high H<sub>2</sub>/SF<sub>6</sub> selectivity of over 6800 and 12000, respectively. However, SF<sub>6</sub> is a large species and high selectivities are expected. Generally, it was demonstrated that the silica network size was enlarged when the number of phenyl groups on the silicon source increased because larger spaces surrounded the aromatic moieties. However, in the latter investigation and many others cited above, the measurement of He, H<sub>2</sub> and Ne were not carried out, and this determination is crucial for determining the permeation mechanism and whether pores are actually present [38].

In this study silica membranes are prepared on porous alumina substrates (60 nm) by employing the CVD of vinyltriethoxysilane (VTES), a precursor that has not been studied before, to investigate the effect of the vinyl group on the silica structure and stability of the membrane. Scanning electron microscopy (SEM) and in situ Fourier transform infrared (FTIR) measurements were used to characterize the morphology and structure of the membrane after CVD. There have been many recent papers dealing with organic-silica hybrids, but the vast majority of these do not present spectroscopic characterization of the organic moieties. A few studies in which infrared spectroscopy was used are mentioned here. Meng et al. prepared organosilica membranes using BTESE-TEOS mixed precursors by the sol-gel method to control the pore sizes of organosilica networks [39]. The formation of a partially cross-linked polysiloxane structure with hydrocarbon unit in a BTESE-TEOS-derived silica network was confirmed by FTIR spectrometry. Lee et al. prepared organosilica membrane using TEDMDS by the sol-gel method [31]. The methyl groups were confirmed after firing at 823 K in a nitrogen atmosphere by FTIR measurement, but the methyl group combusted at 823 K in air. This study demonstrates a general in situ FTIR method which allows observation of the organic functionalities. The permeation properties, including those of He, H<sub>2</sub>, and Ne, hydrothermal stability, and permeation mechanism of the prepared membranes are discussed in detail.

## 2. Experimental

### 2.1. Preparation and characterization of VTES-derived silica membrane

The VTES-derived silica membrane in this work consisted of three layers: a macroporous  $\alpha$ -alumina support, a  $\gamma$ -alumina intermediate layer and a VTES-derived silica layer. A commercial porous  $\alpha$ -alumina support was used (Noritake Corporation, O.D. = 6 mm, I.D. = 4 mm, length = 30 mm, nominal pore size = 60 nm) which was attached to non-porous alumina tubes using glass joints obtained by melting a glass paste (Nippon Electric Glass Co., Ltd) at 1273 K for 10 min.

The  $\gamma$ -alumina intermediate layer was prepared by a dipping-calcining method on the macroporous  $\alpha$ -alumina support. First, the outside of the support was wrapped with Teflon, then the tube was immersed into a dipping solution containing a boehmite sol of size 80 nm for 10 s, and finally the tube was dried in air for 6 h. Following this, the

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