



Fabrication of silicon carbide membranes on highly permeable supports



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ARTICLE INFO

Keywords:

Inorganic membrane
Silicon carbide
Nanoporous
AHPCS
Gas separation
Slip-casting
Dip-coating

ABSTRACT

We have recently reported (Wangxue Deng, Xinhai Yu, Muhammad Sahimi, and Theodore T. Tsotsis, Highly permeable porous silicon carbide support tubes for the preparation of nanoporous inorganic membranes, *J. Membr. Sci.* 2014, 451, 192–204) on the preparation of highly permeable and mechanically strong porous SiC tubular supports via the pressureless sintering of β -SiC powders, for potential use in the fabrication of nanoporous SiC membranes. In the paper, the effect of the type of starting powders used and their composition, the sintering temperature and the amount of sintering aids utilized on the transport characteristics and the surface roughness of these supports were systematically investigated. These tubular SiC supports exhibit very high fluxes (a He permeance as high as $\sim 6 \times 10^{-5} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$) compared to supports prepared previously by our group and others, and are also mechanically strong to withstand the pressure drops required in their use as membrane supports. In this study, we report on the use of these supports in the preparation of SiC nanoporous membranes. The task of preparing high-quality membranes using these substrates is made possible via the use of a technique that creates on the support an interlayer scaffold made of highly uniform SiC nanopowders, followed then by the deposition of the SiC precursor layers. Utilizing these newly developed highly permeable, yet mechanically strong, silicon carbide supports, nanoporous silicon carbide membranes were fabricated, with permeances which are an order of magnitude higher than membranes prepared with less permeable supports but with comparable separation characteristics.

1. Introduction

Membrane separations have attracted attention over the past three decades due to their low energy requirements compared to the more conventional separation technologies like distillation. Polymeric membranes have been the most intensively investigated, and are now widely used commercially. Inorganic membranes, on the other hand, have received relatively less attention, despite the fact they also show good promise for broad applications [1–5]. There are presently a number of commercial liquid-phase separations employing such membranes, but commercial gas-phase applications are presently lacking. However, high-temperature and high-pressure gas-phase reactive separations are an area where inorganic membranes have, potentially, a distinct advantage over polymeric membranes, and thus such applications remain today key drivers for the further development of inorganic membranes. In particular, hydrogen-selective inorganic membranes for use in the efficient production of hydrogen, whose demand has been increasing steadily in recent years due to its potential use in clean energy generation, are attracting significant attention [6].

Each class of inorganic membranes under consideration today has

its own unique range of potential applications. Pd and Pd-alloy membranes, for example, have exceptionally high selectivities and are today being considered for use in the production of ultra-pure hydrogen streams (e.g., [6,7]). Microporous silica (e.g., [8–10]) and carbon molecular sieve (CMS) membranes (e.g., [11–13]) are also highly permeable to hydrogen, though their selectivity is not necessarily as high as that of metal membranes (which, in principle, should be totally impermeable to all other gases but hydrogen). Their costs, on the other hand, are reported to be relatively lower than that of Pd membranes, and they are also thought to be better suited for large-scale applications because they do not raise concerns about the limited availability of the metal. They are, as a result, receiving attention today in hydrogen production [6] and energy storage applications [14]. All these membranes, however, face challenges when used in reactive separations for hydrogen production in the context of power generation [6,7], because of concerns about hydrothermal stability (silica), high cost and sensitivity to sulfur poisoning and coking (metal membranes), and concerns about exposure to oxidizing environments (CMS membranes).

This has then necessitated the search for alternate materials to prepare these membranes with. A different type of hydrogen-perme-

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lective microporous membrane, which shows promise in overcoming some of these challenges, is made of materials with a $[-\text{Si-C}]$ - backbone [15–33], because of their many desirable unique properties, like high corrosion resistance [34], high thermal conductivity [35], high thermal shock resistance [36], and excellent chemical and mechanical stability [37].

To prepare such membranes, two different preparation techniques have been employed: chemical-vapor deposition (CVD)/chemical-vapor infiltration (CVI), and the pyrolysis of pre-ceramic polymer precursors. Early efforts [15–17], employing the CVI/CVD technique and alumina porous supports prepared SiC membranes with mostly Knudsen-type transport characteristics, and no permselectivity towards hydrogen. Ciora et al. [18] were the first to report on the preparation of truly microporous SiC membranes on $\gamma\text{-Al}_2\text{O}_3$ tubular supports via the CVD technique by employing two different CVI/CVD precursors, namely $\text{CH}_3\text{SiH}_2\text{CH}_2\text{SiH}_3$ (1,3-disilabutane or DSB) and $(\text{C}_3\text{H}_7)_3\text{SiH}$ (TPS). Both precursors produced hydrogen permselective membranes [18]. However, the DSB-derived membranes, though thermally stable, were hydrothermally unstable. The TPS-derived SiC membranes, on the other hand, proved stable in the presence of high-pressure (1–3 bar) and high-temperature ($< 750^\circ\text{C}$) steam, which makes them good candidates for potential application in hydrogen production via the steam reforming of methane and other hydrocarbons. However, the preparation procedure using TPS involved multiple steps, and required a high temperature ($\sim 1000^\circ\text{C}$) post-treatment [18], which impacted the membrane's pore structure, thus making it difficult to predict and to control final product quality, and from a membrane manufacturing standpoint also diminishing the advantage of the on-line control of the CVD/CVI technique.

As a result, the Group abandoned the CVD/CVI approach [18], in favor of a method that involved depositing thin pre-ceramic polymer films on macroporous SiC supports followed by pyrolysis in an inert atmosphere (Ar) to produce a SiC microporous ceramic. The precursor utilized was allyl-hydridopolycarbosilane (AHPCS), a partially allyl-substituted hydridopolycarbosilane (HPCS). HPCS and AHPCS both produce a SiC-based ceramic with a (Si/C) ratio close to one [19,20]. However, the allyl groups present in the AHPCS promote polymer cross-linking in Ar, rather than oxygen, which is typically utilized for other PCS polymers. This is important, since curing in oxygen may introduce a substantial fraction of $[-\text{Si-O-C}]$ - linkages in the bulk of the resulting ceramics, which have proven to be thermally and hydrothermally unstable [21,22]. The initial efforts employed [18] a simple dip-coating method to deposit the thin precursor films, and prepared membranes with a satisfactory H_2 permeance (in the range 10^{-8} – 10^{-7} $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$), but relatively low selectivity (an ideal separation factor of ~ 20 for He/N_2 at 200°C). Subsequently, the Group improved the preparation method by augmenting the dip-coating process with a slip-casting step (with the aid of SiC nanopowders or nanofibers) that conditions the support surface prior to film deposition [38,39]. Combining slip-casting with dip-coating significantly improved membrane properties, but equally importantly the reproducibility in preparing high-quality membranes. Also, steam-stability experiments with the membranes lasting 21 days, using an equimolar ($\text{He}/\text{H}_2\text{O}$) mixture at 200°C , indicated good membrane stability at these conditions. (We envision in our Group the primary use of SiC membranes being in reactive separations for hydrogen production, in the context of power generation via the Integrated Gas Combined Cycle (IGCC) [7,11–13,40]. In such an application, the membrane reactor treats the off-gas of the coal (biomass)-gasifier via the water gas shift reaction (WGS) in order to produce in situ a pure hydrogen stream for power generation as well as a high-pressure CO_2 stream ready for sequestration and storage. We employ low-temperature shift (LTS) catalysts which, typically, operate in the temperature range of 175 – 300°C).

The preparation technique was further improved [41], by alternating the dip-coating of the SiC precursor layers with coatings of

polystyrene sacrificial interlayers on the top of slip-casted SiC supports. Membranes prepared by this technique exhibited (He/Ar) and (H_2/Ar) ideal separation factors in the range of (176–465) and (101–258), respectively, with permeances 2–3 times higher than those prepared by the more conventional techniques [39]. Mixed-gas experiments with the same membranes indicate separation factors as high as 117 for an equimolar (H_2/CH_4) mixture. This superior performance was attributed [41] to the effect that PS has on the formation of the three-dimensional (3-D) membrane pore structure during AHPCS pyrolysis, and its role in preventing the pre-ceramic polymer macromolecules from infiltrating into the underlying membrane layers during dip-coating.

Prior to the publication by this group [18], other investigators had also reported the preparation of $[-\text{Si-C}]$ - type porous membranes via the pyrolysis of thin films made from a variety of other precursors (e.g., PCS and polysilanes). In an early effort, Morooka and coworkers [21,22] pyrolyzed PCS, cured in oxygen, to prepare $[\text{Si-O-C}]$ membranes on alumina substrates, using polystyrene (PS) as a pore former. A membrane prepared with 1% PS in PCS had a H_2 permeance of 4×10^{-8} $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, and an ideal H_2/N_2 selectivity of 20 at 773 K; however, it proved unstable when heated in Ar at 1223 K, or exposed to steam at 773 K. Lee and Tsai [24,25] prepared $[\text{Si-O-C}]$ membranes by pyrolysis of polydimethylsilane (the PMS layer was subjected to a thermolytic reaction at 733 K in Ar, followed by O_2 curing at 473 K, and finally pyrolyzed at various temperatures from 523 to 1223 K). The membranes prepared via pyrolysis at 873 K had the best separation characteristics (membranes prepared at the higher temperatures were not microporous), exhibiting a H_2 permeance of $\sim 2.7 \times 10^{-9}$ $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, and an ideal (H_2/N_2) selectivity of 20 at 473 K. PMS-derived membranes prepared in an autoclave under a N_2 atmosphere at low temperatures were also microporous, but proved unstable to the exposure to steam [26].

Subsequent to these earlier efforts (and the study of Ciora et al. [18]), other Groups have reported efforts to produce nanoporous SiC membranes via the pyrolysis of precursor films. Wach et al. [27,28] prepared $[\text{Si-O-C}]$ membranes by the pyrolysis of a blend of PCS and polyvinylsilane films on porous alumina substrates by radiation curing in the presence of O_2 . Their membrane exhibited a H_2 permeance of $\sim 3 \times 10^{-9}$ $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ and ideal (H_2/N_2) and (He/N_2) selectivities of 206 and 241 at 250°C , respectively [28]. Suh et al. [23] spin-coated thin HPCS films on flat γ -alumina substrates to prepare, upon pyrolysis, SiC membrane films with H_2 permeances as high as 1.6×10^{-7} $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, and with (H_2/N_2) permselectivity of > 42.5 at room temperature. To reduce the fraction of $[\text{Si-O}]$ bonds in the structure of the resulting membranes, several studies have attempted curing the PCS films in the absence of O_2 . For example, Suda et al. [30,31] prepared SiC membranes by dip-coating PCS on macroporous α -alumina tubes, using p-diethynylbenzene (as a cross-linking agent) and $\text{Pt}_2(\text{dvs})_3$ (dvs: 1,3-divinyltetramethyldisiloxane) as a hydrosilylation catalyst (PS was used as a pore-former in the preparation of some of these membranes). Their cross-linked PCS-derived SiC membranes exhibited ideal (H_2/N_2) separation factors of (90–150) and a H_2 permeance in the range of $(1-3) \times 10^{-8}$ $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ at 373 K [30]. Nagano et al. [32] prepared SiC membranes by dip-coating of PCS on γ -alumina supports, and reported a H_2 permeance of $\sim 10^{-7}$ $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, and an ideal separation factor of (8–12) for H_2/N_2 at 873 K. However, curing of PCS in the absence of oxygen resulted in a high carbon ratio in the final membranes [32]. The same group applied a hybrid approach involving using a CVI technique (operated in a cyclic fashion, by switching between $\text{SiH}_2\text{Cl}_2 + \text{H}_2$ and $\text{C}_2\text{H}_2 + \text{H}_2$) to repair pinholes and cracks on membranes prepared via the pyrolysis of PCS films coated on γ -alumina substrates; however, not much improvement was reported for the H_2/N_2 permselectivity [33]. Takeyama et al. [42] prepared SiC membranes by dip-coating a PCS layer on alumina tubes ($\alpha\text{-Al}_2\text{O}_3$ coated with a thin $\gamma\text{-Al}_2\text{O}_3$ layer), exposing the coated film to electron beam irradiation in He at room temperature, followed by subsequent pyrolysis at a preset temperature (973 K, 1073 K, and

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