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Nanostructured ZrO_2 membranes prepared by liquid-injection chemical vapor deposition

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ABSTRACT

Using the molecular compound $Zr(OBu^t)_4$ in a liquid-injection chemical vapor deposition process, microporous zirconia membranes were deposited on porous multi-layered alumina substrates consisting of a macroporous α-alumina base covered with a mesoporous γ-alumina layer. The structure of nanocrystalline zirconia (ZrO_2), membranes formed by the thermal decomposition of the precursor varied depending on the decomposition temperature and the injection frequency. The deposited zirconia membranes were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and atomic force microscopy (AFM). X-ray diffraction analysis patterns of the deposits obtained at 500 and 600 °C indicated a mixture of tetragonal and monoclinic ZrO_2 phases, whereas the fraction of the monoclinic phase increased at higher substrate temperature and injection frequency. Morphology and surface roughness are strongly dependent on the process parameters. ZrO_2 membranes prepared by the liquid-injection chemical vapor deposition had a microporous structure with less than 1 nm Kelvin diameter. The liquid-injection chemical vapor deposition is a unique method to prepare microporous membranes in one step without any post-treatment.

1. Introduction

Inorganic membranes are highly promising candidates for use in current separation technology, particularly at high temperatures and in chemically harsh environments [1–3]. Substantial amount of reported work has shown that microporous inorganic membranes possess unique perm-separation properties for gases and liquids unattainable by polymeric gas separation membranes [4–8].

By the common sol–gel route, inorganic membranes are prepared by casting colloidal particles onto a porous substrate structure [9–12]. The process often requires clean room conditions to avoid pinholes due to dust particles. The coating and drying processes are repeated, generally, followed by calcination. Another approach are gas phase techniques such as chemical vapor deposition, CVD. In the CVD approach, gaseous precursors are introduced and after thermal decomposition a solid deposit is formed on the porous substrate or in the pores of the substrate. Microporous membranes can be obtained by one-step synthesis. Liu and co-workers reported pore narrowing of commercial 4 nm pore γ-alumina membrane tubes by CVD of silica using tetraethoxysilane (TEOS) and oxygen as starting materials [13,14]. Morooka and co-workers modified 6–9 nm pore γ-Al_2O_3 membranes by a similar process [15,16]. However, due to a lack of adequate precursors, this method is mainly limited to silica.

State-of-the art microporous silica membranes are for example very selective in hydrogen separation. However their chemical resistance is rather limited and their hydrothermal stability is still insufficient for applications such as steam reforming [17]. Therefore, the development of new inorganic membrane systems is an interesting and important challenge. Given the high mechanical strength, thermal stability and chemical inertness of zirconia, it has high relevance as a membrane material. Zirconia can be used for aqueous filtration and offers much better alkali durability than other ceramic membranes, such as silica [18]. In addition, zirconia membranes allow steam sterilization and cleaning with caustic solution [19].

Metal–organic chemical vapor deposition (MOCVD) is an attractive technology for the deposition of thin ZrO_2 films that offers low

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deposition temperatures, microstructure control of the deposited material and homogeneous deposition on three-dimensional substrates [20,21]. Furthermore, the use of specifically designed molecular (single-source-) precursors with an elemental composition equal to that of the condensed matter allows the deposition of films with correct stoichiometry and high purity. For the deposition of ZrO_2 by MOCVD the range of suitable precursors includes β-diketonates [22–24], fluorinated β-diketonates [24–25], metallocene and amide complexes [26,27] as well as alkoxides [28–35]. Although the alkoxide zirconium-*tert*-butoxide, $Zr(OBu^t)_4$, shows sufficient volatility to be suitable for decomposition and formation of ZrO_2 films in the conventional thermal MOCVD process [36], the use of a liquid-delivery system for the precursor implies several advantages: In liquid-injection MOCVD the solvent vapor is the major gas phase species and the concentration of the precursor in the gas phase is directly related to the concentration of the precursor in the liquid solution inducing an easy control of vapor pressure and precursor concentration in the gas flow. Furthermore, the flow rate is fixed by the opening frequency and time of the piezovalve between vaporizer and reaction chamber offering the controlled supply of precursor to reaction zone. This allows a simple control of film thickness by the number of injections. In addition, the precursor reservoir remains cold up to the point where the solution is vaporized avoiding any unwanted aging of the precursor, which is considered as a benefit for up-scalability and economical aspects [37].

Thus, for these reasons the use of liquid-injection MOCVD is a promising approach for the preparation of new nanostructured zirconia membranes from the molecular precursor $Zr(OBu^t)_4$ on porous multi-component substrates consisting of a macroporous α-alumina base covered by a mesoporous γ-alumina layer.

In this work, the precursor $Zr(OBu^t)_4$ has been chosen due the presence of pre-formed Zr–O bonds having a covalent character and favoring the formation of ZrO_2 at low processing temperatures without any additional source of oxygen [36]. The use of such single molecular sources simplifies the growth procedure significantly and allows a precise control over phase composition and particle size of the films [38–42]. The thermal decomposition of the precursor in liquid-injection MOCVD process was investigated as a function of substrate temperature and injection frequency that allowed tuning the crystalline phase, film thickness and density of the as-deposited zirconia.

2. Experimental

2.1. Substrate preparation

Disk shaped α-Al_2O_3 substrates (39 mm diameter and 2.3 mm thickness) were prepared by slip casting technique using α-Al_2O_3 powder (AKP-30, Sumitomo Chemical Co., Tokyo, Japan). The final sintering temperature was 1100 °C. A mesoporous γ-Al_2O_3 layer was applied on the α-Al_2O_3 substrates by dip-coating. Boehmite sols were prepared by mixing 0.5 mol of aluminum-tri-sec-butoxide (ATSB; 97% purity, Acros. Geel, Belgium) into 70 mol of distilled water at 90 °C under vigorous stirring followed by precipitation with 1 M HNO_3 (E. Merck, Darmstadt, Germany) to a pH of 2.5. The result is a stable boehmite sol with a clear and limpid blue-white appearance. A dip-coating solution was obtained by diluting 30 ml of boehmite sol with 20 ml of a solution (0.05MHNO_3) containing 0.6 g of polyvinyl alcohol (PVA). The solution was filtered through a 0.8 μm cellulose acetate filter (Model FP 030/50, Green Rim, Schleicher and Schuell GmbH, Dassel, Germany) to remove larger particles from the sol before the sol was cast on the surface of polished α-Al_2O_3 substrates by dip-coating. After dip-coating, substrates were dried and fired at 600 °C for three hours with a heating/cooling rate of 1 K/min. In order to suppress eventual pinholes and small defects, the described deposition process was repeated resulting in a γ-Al_2O_3 layer with a pore size of 2–3 nm and a thickness of 3–5 μm.

2.2. Synthesis of $Zr(OBu^t)_4$ precursor

The synthesis of $Zr(OBu^t)_4$ precursor and its manipulation were performed in a modified Schlenk type vacuum assembly, taking stringent precautions against atmospheric moisture. All solvents were purified by standard methods and stored over appropriate desiccating agents. The compound zirconium *tert*-butyloxide ($Zr(OBu^t)_4$) was synthesized by a metathesis reaction of lithium diethyl amide with zirconium chloride followed by a ligand exchange reaction with an excess of Bu^tOH as described in the literature [43–45]. The obtained $Zr(OBu^t)_4$ was purified by distillation under reduced pressure (50 °C/10^{-2} Torr).

2.3. Deposition of the ZrO_2 membranes by liquid-injection MOCVD

Fig. 1 shows a scheme of the liquid-injection MOCVD reactor used in this study. The precursor solution was introduced form the reservoir through a pressurized line (100 mbar primary pressure) into the vaporizer, whose temperature was set to 60 °C. Thereafter, precursor injection followed under controlled argon flow through a piezovalve into the quartz reaction chamber. Generally, argon is used for the active transport of the precursor in vapor or droplet form to the substrate. For precursor compounds with very low vapor pressures a high flow of argon is required to avoid the deposition of the precursor at the wall of the heated vaporizer line. In this study, the argon flow was not varied during the experiments, but was fixed to a value of 50 sccm (at 25 °C, 1 atm), which was high enough for efficient deposition rates. Further, the system can be either pressurized with argon or be connected to the vacuum, which allows the removal of air and water traces prior to the application of air and moisture sensitive precursors such as $Zr(OBu^t)_4$. The alumina substrate was inductively heated in a range of 500–600 °C using a graphite susceptor. The amount of injected precursor depends on concentration of the precursor solution, injection frequency, opening times of the piezovalve and argon flow rate. In the present study a solution of 2 vol% $Zr(OBu^t)_4$ in toluene was used to deposit thin ZrO_2 films on the alumina substrates. The precursor solution was injected for 30 min with 1 Hz, respectively 2 Hz injection frequency by a constant opening time of the piezovalve of 1 ms for all experiments. Herein, the injection frequency refers to the opening interval of the piezovalve. Using an injection frequency of 1 Hz and a set opening time of 1 ms, the valve opens for 1 ms every second, respectively for 2 ms

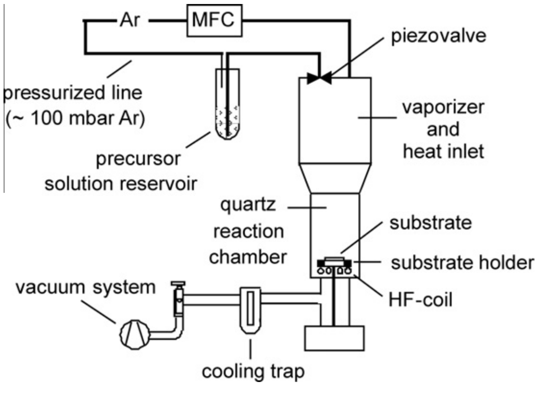

Fig. 1. Scheme of the liquid-injection CVD reactor.