



# Facile synthesis of zirconia doped hybrid organic inorganic silica membranes



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## ABSTRACT

Hybrid organic inorganic silica membranes are interesting candidates for gas-separation applications due to their excellent hydrothermal stability. However, up to now these membranes lack the separation performance required to separate hydrogen from carbon dioxide. In this work a procedure for doping zirconia into the hybrid silica matrix is reported, resulting in an improved H<sub>2</sub>/CO<sub>2</sub> permselective membrane compared with non-doped hybrid silica membranes. Zirconia doped 1,2-bis(triethoxysilyl)ethane (Zr-BTESE) was synthesized by sol–gel chemistry, using zirconyl nitrate as the zirconium source. By optimization of the sol reaction conditions (i.e. reaction time and temperature) a homogenous sol was obtained. Defect-free membranes were obtained by adjusting the concentration of the dip-coating solution. The doped membranes showed a slight decrease in hydrogen permeance from  $4.4 \times 10^{-7}$  to  $1.8 \times 10^{-7}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> as compared to an undoped BTESE membrane, but a large increase in H<sub>2</sub>/CO<sub>2</sub> (from 4 to 16) and H<sub>2</sub>/N<sub>2</sub> (from 12 to 100) permselectivity was observed.

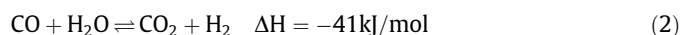
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## 1. Introduction

The world energy demand is increasing and although the growth in energy produced by renewable sources is large, there is still a big demand for energy from coal and gas, according to the energy outlook of the EIA [1]. This demand for fossil fuels will cause a further increase in carbon dioxide emissions. According to the 4th IPCC assessment report carbon dioxide is one of the main contributors to global warming [2]. It is therefore necessary to reduce the emissions of CO<sub>2</sub> by means of carbon capture and storage (CCS). One of the strategies for CCS is pre-combustion carbon capture in which a fuel is converted to hydrogen and carbon dioxide that can be separated easily.

Methane steam reforming (MSR), as given in reaction (1) can be utilized to convert natural gas to hydrogen and carbon monoxide, a mixture called synthesis gas or syngas. This syngas is shifted towards hydrogen and carbon dioxide in the water gas shift reaction (WGS) (2). Due to the highly exothermic nature of the WGS reaction it is often performed in a two-stage approach to ensure full conversion of carbon monoxide to hydrogen and CO<sub>2</sub> [3]. A typical purification step to obtain 90% pure hydrogen for pre-combustion carbon capture is physical absorption of carbon dioxide, e.g. by using Selexol and Rectisol [4]. For applications that demand high

purity hydrogen like ammonia synthesis or fuel cell applications typically pressure swing adsorption is used [3].



By using a water gas shift membrane reactor (WGS-MR) instead of the conventional approach, the equilibrium of the WGS reaction (2) can be shifted to the product (H<sub>2</sub> and CO<sub>2</sub>) side by continuous removal of hydrogen. The need for extra cooling steps is eliminated by the integration of reaction and separation into one unit operation. This reduces the energy demand, resulting in a more efficient process.

Membranes that are utilized in a WGS-MR need to have a high hydrogen permeance and a high H<sub>2</sub>/CO<sub>2</sub> selectivity. Palladium membranes have a high H<sub>2</sub>/CO<sub>2</sub> selectivity and high hydrogen permeance, but suffer from hydrogen embrittlement and sulfur poisoning, which decreases their lifespan [5]. On the other hand sol–gel derived silica membranes are known for their excellent H<sub>2</sub>/CO<sub>2</sub> selectivity, but degrade in a hydrothermal environment due to the mobility of the silanol groups in the material [6,7]. Strategies to increase the hydrothermal stability of silica are doping silica with metal oxides to stabilize the siloxane bonds [6,8–11] or by using a hydrophobic compound to prevent water sorption onto or into the material [12–14]. The latter approach is used in hybrid silica membranes based on bridged silsesquioxanes like

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bis(triethoxysilyl)ethane (BTESE). It is proven that BTESE membranes are hydrothermally stable for over one year in dehydration of butanol by pervaporation at 150 °C [15]. These BTESE derived membranes have a lower H<sub>2</sub>/CO<sub>2</sub> selectivity than silica membranes. Kanezashi et al. [16] proposed that the network of BTESE is more loose due to the ethane bridge, which would lead to a larger pore size. From silica it is known that an increase in calcination temperature from 400 °C to 600 °C leads to densification of the matrix and a lower number of silanol groups, which leads to an increase in H<sub>2</sub>/CO<sub>2</sub> selectivity from 7.5 to 71 [17]. Since BTESE starts to decompose above 470 °C in an inert atmosphere [12] only temperatures below this decomposition temperature can be used for calcination. Typical calcination temperatures for BTESE are 300 °C [12,16], which leads to a less condensed network and hence to a lower H<sub>2</sub>/CO<sub>2</sub> selectivity if compared with silica membranes calcined at 600 °C.

In order to increase the gas separation performance of these hybrid silica systems two routes have been suggested. The first route is changing the length of the organic bridge in the silsesquioxane [18], while the second route is metal doping of the hybrid silica matrix [19]. Metal doping of silica with niobium, cobalt or nickel was used by several research groups to improve the hydrothermal stability [9,11,20–24] and was only recently used on BTESE to improve the gas separation performance. Qi et al. doped BTESE with niobia to achieve a H<sub>2</sub>/CO<sub>2</sub> selectivity of 200 [19]. The authors explained this improved selectivity by network densification, caused by niobia, and by a reduced affinity for CO<sub>2</sub> due to the presence of acidic niobia groups in the niobia/BTESE network.

Zirconia doping of silica by using a zirconium-alkoxide was done by Yoshida et al. [24]. They observed that increasing the zirconia content in silica results in increased activation energy of permeation for helium and hydrogen. This increased activation energy is ascribed to network densification, which leads to smaller pore sizes. This results in lower gas permeances but also in a higher selectivity for hydrogen over carbon dioxide.

In this work a zirconia doped hybrid silica sol was produced by using zirconyl nitrate as a zirconium source. Zirconyl nitrate was chosen instead of a zirconium-alkoxide precursor due to the too fast hydrolysis rate of the latter. Membranes were prepared by dip coating of the sol on a porous support. The effects of sol concentration in the dip coat solution on membrane microstructure and membrane performance were investigated. The results are compared with undoped BTESE membranes fabricated in a similar way.

## 2. Experimental

### 2.1. Sol-gel preparation

All chemicals were used as received. The hybrid silica precursor, 1,2-bis(triethoxysilyl)ethane (BTESE 97%), was obtained from ABCR. A zirconyl nitrate solution (ZrO(NO<sub>3</sub>)<sub>2</sub> (99%, 35 wt.% in dilute nitric acid) was obtained from Sigma-Aldrich. Ethanol (99%) and concentrated nitric acid (65%) were obtained from Merck.

BTESE sols were prepared by the following procedure: 1.04 mL of a 1.77 mol/L HNO<sub>3</sub> solution was added to 5.53 mL ethanol and placed in an ice bath. Subsequently 3.33 mL of BTESE was dropped slowly into the mixture under vigorous stirring to obtain a final ratio of BTESE:EtOH:HNO<sub>3</sub>:H<sub>2</sub>O of 1:10.8:0.2:6. The mixture was reacted at 60 °C for 90 min and put in an ice bath to quench the reaction. Ethanol was added to the solution to dilute the sol for dip coating to a final silicon concentration of 0.3 mol/L.

Zirconia doped BTESE sols were made by the following procedure: zirconyl nitrate (0.802 mL), 0.337 mL H<sub>2</sub>O and 5.53 mL ethanol were mixed and the mixture was placed in an ice bath. BTESE

(3.33 mL) was added drop wise to the mixture under vigorous stirring to obtain a final ratio of BTESE:ZrO(NO<sub>3</sub>)<sub>2</sub>:EtOH:HNO<sub>3</sub>:H<sub>2</sub>O of 1:0.19:10.5:0.2:6. The mixture was reacted at 25 °C for 90 min and afterwards put in an ice bath to quench the reaction. Ethanol was added to the solution to dilute the sol for dip coating. Final [Zr + Si] concentrations were 0.33 mol/L, 0.2 mol/L and 0.13 mol/L with a Si:Zr ratio of 10:1. All sol solutions were stored at –18 °C prior to further use.

### 2.2. Characterization

The sol particle size was determined by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS. Diluted sols were used for the measurements and were filtered over a 0.2 μm filter beforehand to remove dust-particles that could have a negative influence on the measurement.

Unsupported membrane materials were obtained by drying the sol overnight in a petri dish. After drying, the flakes were calcined under nitrogen. Calcination was performed at 400 °C or 600 °C with a heating/cooling rate of 0.5 °C/min and a dwell of 3 h. After calcination the flakes were ground into a powder using a mortar. Unsupported silica, prepared by the procedure as described by De Vos and Verweij [17], was used for comparison. These powders were calcined at 600 °C in air with a heating/cooling rate of 0.5 °C/min and a dwell of 3 h.

Nitrogen adsorption experiments were performed on unsupported membrane materials with a Quantachrome Autosorb-1MP. The samples were degassed overnight at 300 °C. The surface area of the samples was calculated using the BET equation and the micropore volume was calculated using the Dubinin–Radushkevich method [25]. Powder X-ray diffraction was performed on a Bruker Phaser D2. Scans were taken from 2θ of 20° to 80° with a step size of 0.02° and a step time of 0.5 s. Thermogravimetric analysis was performed on a Netzsch STA 449 F3 Jupiter with a nitrogen flow of 70 ml min<sup>-1</sup>. Measurements were taken with a heating rate of 20 °C/min from 35 °C to 1000 °C. Pretreatment was done at 50 °C in vacuum to ensure that most of the physisorbed water is removed.

### 2.3. Membrane preparation

Porous α-alumina supports (pore size 80 nm, porosity 35%) with a diameter of 39 mm and a thickness of 2 mm (Pervatech B.V. the Netherlands) were coated twice under cleanroom conditions with a boehmite sol and calcined at 650 °C at a heating rate of 1 °C/min and a dwell of 3 h, resulting in a γ-alumina intermediate layer with a thickness of 3 μm and a pore size of 5 nm as reported by Uhlhorn et al. [26]. BTESE and Zr-BTESE layers were coated in one step under cleanroom conditions onto the supported γ-alumina membranes using an automatic dip-coating machine, with an angular dipping rate of 0.06 rad s<sup>-1</sup>. The membranes were calcined under nitrogen at 400 °C with a heating and cooling rate of 0.5 °C/min and a dwell of 3 h. Zr-BTESE membranes were named Zr-BTESE-X in which X is the total [Si + Zr] concentration in mol/L in the dip coating solution.

High resolution scanning electron microscopy (SEM) was performed with a Zeiss Leo 1550 FESEM on membrane cross-sections to determine the thickness of the selective layer. The cross sections were placed on a sample holder and partly covered with aluminum tape to prevent sample charging. No further pretreatment was done on the samples and images were acquired at an accelerating voltage of 1 kV.

### 2.4. Single gas permeation

The membrane performance was characterized by means of single gas permeation. The membranes were measured in a

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