



Hydrothermal stability of silica, hybrid silica and Zr-doped hybrid silica membranes



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ABSTRACT

Hybrid silica membranes have demonstrated to possess a remarkable hydrothermal stability in pervaporation and gas separation processes allowing them to be used in industrial applications. In several publications the hydrothermal stability of pure silica or that of hybrid silica membranes are investigated. To gain deeper insight into the mechanism of hydrothermal stability of silica-based membranes we report a comparison under identical conditions of the gas permeation performance of silica (TEOS), hybrid silica (BTESE) and Zr-doped BTESE (Zr-BTESE) membranes before and after hydrothermal treatments. First, a fast and straightforward hydrothermal stability test at 100 °C was applied to screen these membranes. The BTESE and Zr-BTESE membranes maintained their excellent performance after this test, though the TEOS membranes lost their selectivity. Second, hydrothermal tests under water gas shift (WGS) conditions were performed at different temperatures. No significant changes in permeance and selectivity were observed for BTESE derived membranes after a hydrothermal treatment at 300 °C. Surprisingly, a large reduction in carbon dioxide permeance was observed for Zr-BTESE hybrid silica membranes after a hydrothermal treatment at 200 or 300 °C, resulting in a significant increase of the H₂/CO₂ permselectivity from 12 to 35.

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1. Introduction

Membranes are an interesting alternative for several conventional separation processes, due to the ability to integrate reaction and separation into one unit. The use of membranes is also more energy efficient, since no phase changes are needed as compared to distillation. Since the separation can be performed at high operating temperatures, when using ceramic membranes, there is less need for heat exchange as compared to adsorptive processes.

Most processes that are of industrial interest for the integration of a membrane separation step, e.g. carbon capture in the production of electricity, often include steam or water vapor at elevated temperatures (180–550 °C). Examples of this are methane steam reforming (MSR, typically performed at 550 °C) and the water gas shift reaction (WGS, typically performed at 180–270 °C). To date one of the best performing ceramic membranes for gas separation applications are microporous silica membranes, made by sol-gel synthesis using tetraethyl orthosilicate (TEOS) as a precursor [1]. However, these membranes are known to be unstable under hydrothermal conditions due to the reactivity of the formed silanol groups. [2,3] The last decade a lot of research was done on hydrothermally stabilizing these silica membranes.

For improving the hydrothermal stability of silica membranes De Vos et al. [2] added methylated silica to the silica system in order to obtain a more hydrophobic membrane and hence to decrease the water adsorption ability. The stability under hydrothermal conditions of these methylated membranes improved if compared with pure silica membranes, but the results were not sufficient for industrial applications, as during pervaporation studies on the dehydration of butanol the lifetime of this newly developed membrane only increased from 25 to 50 days when compared with pure silica membranes [4]. Castricum et al. [5] used 1,2-bis(triethoxysilyl)ethane (BTESE) as a precursor for the fabrication of hybrid silica membranes in order to improve the hydrothermal stability. These hybrid silica membranes showed stable flux values for more than one year in butanol dehydration by pervaporation [4]. So, BTESE derived membranes have shown excellent stability under pervaporation conditions and might be interesting for gas separation applications, to be used under hydrothermal condition. However, the selectivity on gas separation (e.g. H₂/CO₂ or H₂/CH₄) of these membranes is rather low due to the relative open network if compared to TEOS-derived pure silica membranes [6,7]. Recently, we reported zirconia doped BTESE membranes, which show, when compared with undoped BTESE,

an increased hydrogen selectivity towards gases like CO₂, N₂ and CH₄ [8].

In several publications the hydrothermal stability of pure and metal doped silica as well as hybrid silica membranes are investigated [3,9–11]. Unfortunately, a comparison is very difficult to make between these results, as different experimental conditions as well as membrane substrates and intermediate layers are used. To eliminate these factors, in the work as described in this paper, a planar α -alumina substrate coated with γ -alumina was chosen as a starting material, as these supports have a well-defined surface morphology and can be highly-reproducibly fabricated. In this way a fair comparison between the different membrane materials can be made. In this work the focus is on TEOS-derived silica as well as on BTESE and Zr-doped BTESE hybrid silica membranes. The influence of hydrothermal treatment conditions on the gas permeation performance of these membranes is described.

2. Materials and methods

2.1. Membrane fabrication and characterization

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(NO₃)₂ (99%, 35 wt% in dilute nitric acid) was obtained from Sigma-Aldrich. Ethanol (99%). Tetraethyl orthosilicate (TEOS 99%) and concentrated nitric acid (65%) were obtained from Merck.

Silica (TEOS-derived) sols were produced by the method as described by De Vos and Verweij [1]. A one-step sol synthesis was performed at 60 °C for 180 min with a TEOS:EtOH:H₂O:HNO₃ ratio of 1:3.8:6.3:0.085, after which the solution is diluted 19 times prior to coating on the membrane supports. BTESE and Zr-doped BTESE sols were produced by the method as described in detail in [8]. BTESE was synthesized at 60 °C for 90 min with a BTESE:EtOH:HNO₃:H₂O ratio of 1:10.8:0.2:6 and diluted 6 times for coating. Zr-BTESE was synthesized at 25 °C for 90 min with a BTESE:ZrO(NO₃)₂:EtOH:HNO₃:H₂O ratio of 1:0.19:10.5:0.2:6 and diluted 10 times for coating.

Porous α -alumina supports (pore diameter 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 μ m and a pore diameter of 5 nm, as reported by Uhlhorn et al. [12]. TEOS, 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⁻¹. The TEOS-derived silica membranes were fired in air at 600 °C at a heating/cooling rate of 0.5 °C/min and a dwell of 3 h, while the BTESE and Zr-BTESE derived hybrid silica membranes were fired at 400 °C in nitrogen atmosphere at a heating/cooling rate of 0.5 C/min and a dwell of 3 h.

Single gas permeation was performed on an automated setup under nitrogen at 200 °C, see Fig. 1. A feed pressure of 3 bar was applied to the membrane, while the permeate pressure was kept atmospheric. The gases were measured in the following order: helium, nitrogen, methane, hydrogen and carbon dioxide. The permeance of every gas was measured for 30 min to ensure a stable flow. The permselectivity was calculated by the following formula in which F_a is the permselectivity and Q the permeances of the pure gases (x and y):

$$F_a x/y = \frac{Q_x}{Q_y}$$

2.2. Hydrothermal stability tests

A straightforward, relative fast, hydrothermal stability test was developed to screen the membranes. For these tests membranes were placed in a holder a few centimeters above a vessel of boiling water with the silica separation layer facing upwards. The water was heated in a reflux set by an oil bath (T = 110 °C) to ensure the water was boiling (steam temperature 100 °C), but the water was not touching the membrane. These tests in H₂O-saturated stagnant air were continued for 72 h, after which the membranes were removed from the set up and dried at room temperature.

Hydrothermal tests at 200, 300, 400 and 500 °C were performed at atmospheric pressure with a gas composition of 51% v/v H₂O, 34% v/v CO and 15% v/v H₂, which is regarded as the gas phase composition in the water gas shift (WGS) reaction of syngas (CO + H₂). The membranes were placed in a tubular furnace which was flushed with the simulated WGS mixture with a flow of 92 ml/min. These tests were conducted for 72 h, after which the membranes were removed from the furnace and dried at room temperature.

In total 12 different membranes were obtained for further study on gas permeation performance as a way to determine the hydrothermal stability. The samples, including sample codes, as used in this study are summarized in Table 1.

Besides gas permeation tests on the membranes as indicated in Table 1, also *in-situ* hydrothermal treatments were performed in

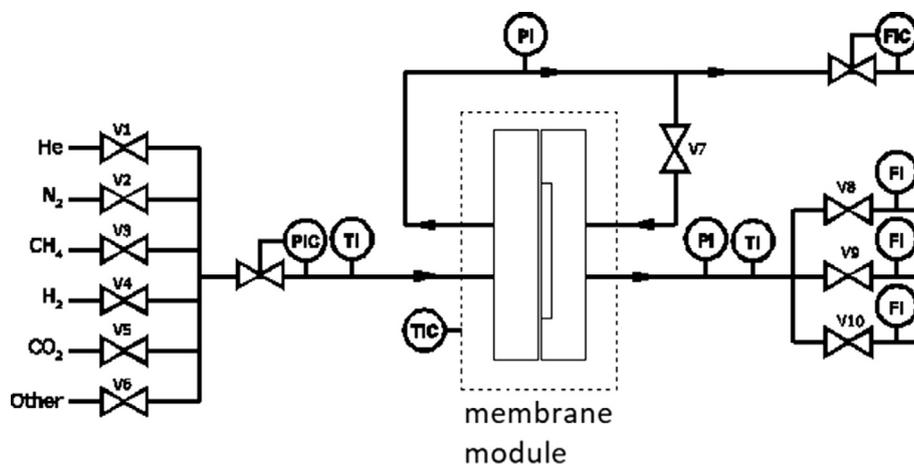


Fig. 1. Schematic presentation of the gas permeation set-up.

Table 1
Membrane samples used.

Sample code	Material	Hydrothermal treatment	
		temperature (°C)	Atmosphere
T	TEOS	–	–
T100	TEOS	100	H ₂ O-Saturated air
B	BTESE	–	–
B100	BTESE	100	H ₂ O-Saturated air
B300	BTESE	300	Simulated WGS*
B400	BTESE	400	Simulated WGS
Z	Zr-BTESE	–	–
Z100	Zr-BTESE	100	H ₂ O-Saturated air
Z200	Zr-BTESE	200	Simulated WGS
Z300	Zr-BTESE	300	Simulated WGS
Z400	Zr-BTESE	400	Simulated WGS
Z500	Zr-BTESE	500	Simulated WGS

* 51% v/v H₂O, 34% v/v CO and 15% v/v H₂.

the gas permeation setup on a Zr-BTESE sample. In this way an eventual change in permeances of the several gases could be investigated as function of time during a hydrothermal treatment. This treatment implies that, after the permeation measurements for all gases were performed at 200 °C under a dry atmosphere, a wet nitrogen flow ($x_{\text{H}_2\text{O}} = 0.01$, corresponding to a steam partial pressure of 1 kPa) of 100 mL/min was passed over the feed-side of the membrane at a pressure of 1 bara for 1 h. After this treatment the membrane was dried in the equipment by a dry nitrogen stream for 10 min at 200 °C before a new permeation measurement was performed. This process of water treatment, followed by drying and permeation analysis, was repeated several times.

Due to limitations in sealing materials in the gas permeation equipment it was not possible to perform high temperature (above 250 °C) in-situ hydrothermal stability tests in this way. Therefore ex-situ tests were chosen to make a comparison between the different membranes.

Finally more insight on the water desorption behavior as a function of temperature was gained by thermogravimetric analysis. For this reason BTESE and Zr-BTESE sols were dried overnight at 20 °C and ground to a powder. The powders were fired using the same temperature program as used for the membranes. Subsequently 0.1 g of the powder was suspended in 5 ml of water and placed in an oven for 16 h at 100 °C. Thermogravimetric analysis was performed on these oven-dried powders, using a Netzsch STA 449 F3 Jupiter with a nitrogen flow of 70 ml/min. Measurements were taken at a heating rate of 5 °C/min from 35 °C to 400 °C.

3. Results and discussion

3.1. Fast hydrothermal stability test

A fast hydrothermal stability test was performed on TEOS-, BTESE-, and Zr-BTESE derived silica membranes in a water-saturated atmosphere at 100 °C. The results of the pure silica (TEOS-derived) membranes are displayed in Fig. 2A where, as function of the gas kinetic diameter the gas permeances are plotted before and after this hydrothermal treatment (T and T100, resp.). Before the hydrothermal treatment, the silica membrane shows excellent permselectivity, which is comparable of what is observed in literature [9]. After the hydrothermal test the performance of these silica membranes changes significantly and shows the same permeance and permselectivity as the γ -Al₂O₃ intermediate layer, which indicates that the selective layer has lost its structural integrity. This phenomenon is also described by other researchers [3,13,14]

In Fig. 2B the gas permeances are displayed for a BTESE derived membrane before and after a hydrothermal treatment at 100 °C (B and B100, resp.). This type of membrane does not show any significant change in permeance after hydrothermal treatment. This hydrothermal stability is in line with the results found for water/alcohol pervaporation at 150 °C, using the same type of BTESE membranes [5]. The results of the Zr-BTESE membranes, before and after a hydrothermal treatment at 100 °C (Z and Z100, resp.), are depicted in Fig. 2C. The permeance of Zr-BTESE derived membranes after hydrothermal treatment (Z100) has dropped slightly, but no significant changes in permselectivity are observed.

The good hydrothermal stability of BTESE-hybrid silica membranes is also reported in many other papers [3,10,11] but the origins of this hydrothermal stability is still unclear. In literature several features are mentioned [15] for the increased hydrothermal stability. Very often the hydrothermal stability is ascribed to an increase of the hydrophobicity or the non-polarity, introduced by the organic groups, resulting in a reduction of the diffusion of water into the membrane. However, the actual hydrophobicity is largely influenced by the molecular organization of the network and Castricum et al. [16,17] showed that the siloxane bonds are still reachable for aqueous species.

A second explanation for the increased hydrothermal stability of these Si-hybrid membranes is the increased ability to connect a monomer with the adjacent network when two silicon atoms are joined by an organic bridge [15]. Organically bridged monomers have a sixfold connectivity while pure silicon only has a four-

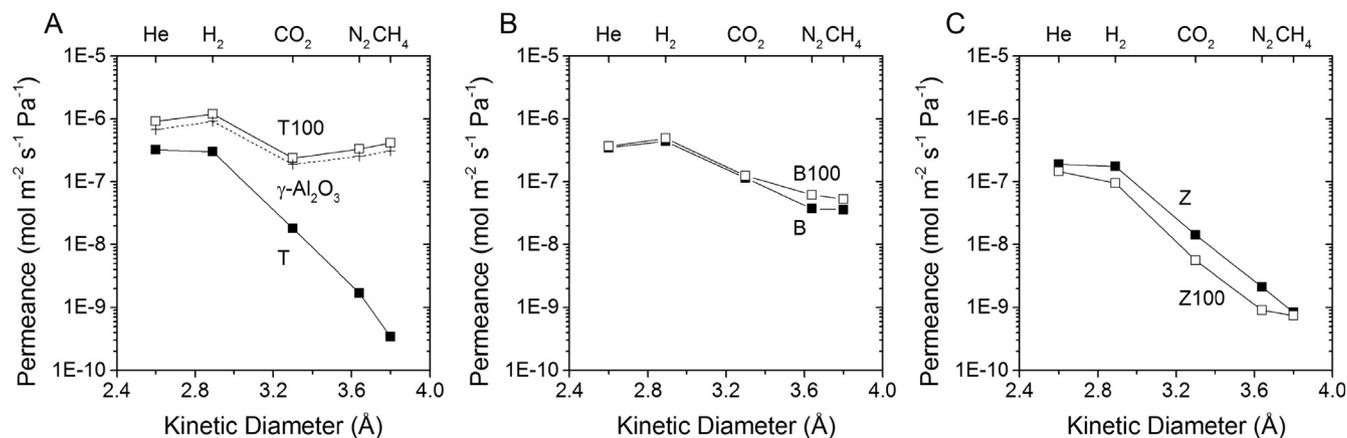


Fig. 2. Gas permeance versus gas kinetic diameter, measured at 200 °C with a transmembrane pressure of 2 bar for TEOS derived silica and γ -Al₂O₃ (A), BTESE derived hybrid silica (B), and Zr-BTESE derived hybrid silica (C) membranes; closed symbols: as prepared membranes; open symbols: after a treatment with boiling water for 72 h.

fold connectivity. To dissolve a monomer all siloxane bonds need to be hydrolyzed and for this reason it is more difficult to dissolve a monomer having a sixfold connectivity than a monomer is having a fourfold connectivity resulting in a significant increase in the hydrothermal stability for organically bridged monomers.

Finally, Ten Elshof et al. [15] added another aspect by considering the improved hydrothermal stability from a more fundamental molecular point of view. Silicon dioxide consist of corner sharing tetrahedra with oxygen atoms at the corner. The Si—O—Si angle between neighboring tetrahedra can vary roughly between 134° and 180° allowing the tetrahedra to move in many different directions. As result of this, also the packing density can increase and incorporation of empty spaces are possible. The BTESE tetrahedral has also a CH₂ segment which is expect to have not the same impressive freedom as the bond angle of the Si—O—Si bound resulting in a lower flexibility of the overall network as compared to the silica network. The incorporation of this organic segment shifts the balance of these interactions and as result of this the hydrothermal stability increases [15,18].

3.2. Hydrothermal stability tests under simulated WGS conditions

From the results, as given in the previous section, it is clear that the pure silica (TEOS-derived) membranes are not interesting to be used under hydrothermal conditions. Therefore, additional hydrothermal tests under a simulated WGS mixture (51% v/v H₂O, 34% v/v CO and 15% v/v H₂) at different temperatures were only performed with BTESE- and Zr-BTESE-derived membranes. The gas permeation results of the non-treated and hydrothermally-treated BTESE membranes are shown in Fig. 3. Here again no significant changes in permeance are observed after a hydrothermal treatment at 300 °C (sample B300).

However, after a treatment at 400 °C (sample B400) lower permeances are observed for helium and hydrogen, which is indicative for densification. In contrast to this, the permeance for nitrogen and methane has increased, which would indicate a pore widening. By looking at these phenomena, it seems that some degradation of the BTESE layer already started to occur at 400 °C. Kappert et al. [19] performed kinetic analyses, by using thermogravimetric measurements, combined with mass spectrometry. In their work it was shown that in an inert atmosphere the onset of decomposition of the ethylene bridge for BTESE-derived membranes is around 500 °C. This onset temperature was determined by using purified

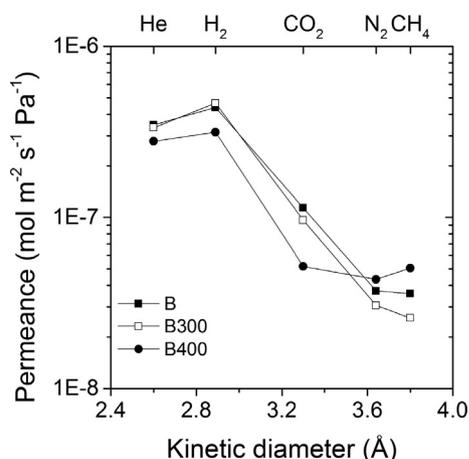


Fig. 3. Permeance versus gas kinetic diameter, measured at 200 °C at a transmembrane pressure of 2 bar, for a pristine BTESE derived hybrid silica membrane (B) and BTESE derived hybrid silica membranes hydrothermally treated for 72 h at 300 or 400 °C under WGS conditions (B300, B400).

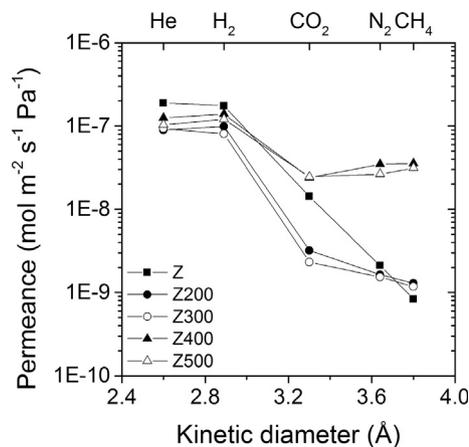


Fig. 4. Permeance versus kinetic diameter measured at 200 °C with a transmembrane pressure of 2 bar for Zr-BTESE derived hybrid silica membranes.

gases and oxygen traps to ensure a complete oxygen-free environment. It is possible that during the hydrothermal treatment, as used in our work some traces of oxygen were still present, which would lower the onset temperature of decomposition. Similar changes in onset temperature were reported in a review paper of Ten Elshof et al. [15], he observed that the in literature reported upper temperature limits varies significantly for the bridging ethylene groups under inert atmosphere from 250 to 500 °C.

The gas permeance results of the Zr-BTESE-derived silica membranes after the hydrothermal stability tests under WGS condition are displayed in Fig. 4. The results show the same increase in nitrogen and methane permeance after a hydrothermal treatment at 400 °C as was observed for BTESE membranes after hydrothermal treatment at 400 °C, described in the previous paragraph (compare Z400 and B400, given resp. in Figs. 2 and 3). Surprisingly, a large drop in carbon dioxide permeance for Zr-BTESE membranes is observed after hydrothermal treatment at 200 and 300 °C (Z200 and Z300) resulting in a significant increase of the H₂/CO₂ permselectivity with almost a factor 3 (see Table 2).

3.3. In-situ hydrothermal stability test under simulated WGS mixture

The static tests, as described before, only give an indication of changes in membrane performance after 72 h of hydrothermal treatment. In this way no information can be obtained how fast the steady state is achieved during such a treatment. In order to investigate the change in gas permeance as function of hydrothermal treatment time, the gas permeance of a Zr-BTESE hybrid silica membrane was measured after 1 h of hydrothermal treatment in the gas permeation equipment at a steam partial pressure of 1 kPa and 200 °C, while this procedure was performed every hour for a total period of 5 h. The results, as given in Fig. 5, depict a significant drop in permeance after one hour of hydrothermal treatment, especially for the smaller gases helium and hydrogen. A steady state is achieved after two hours, No further changes in permeance were observed after two hours of hydrothermal treatment

Table 2
Hydrogen permeance and permselectivity of pristine and hydrothermally treated Zr-BTESE membranes.

Membrane	H ₂ permeance 10 ⁻⁷ mol m ⁻² s ⁻¹ Pa ⁻¹	F _z H ₂ /CO ₂
Z	1.8	12
Z100	0.9	17
Z200	1.0	31
Z300	0.8	35

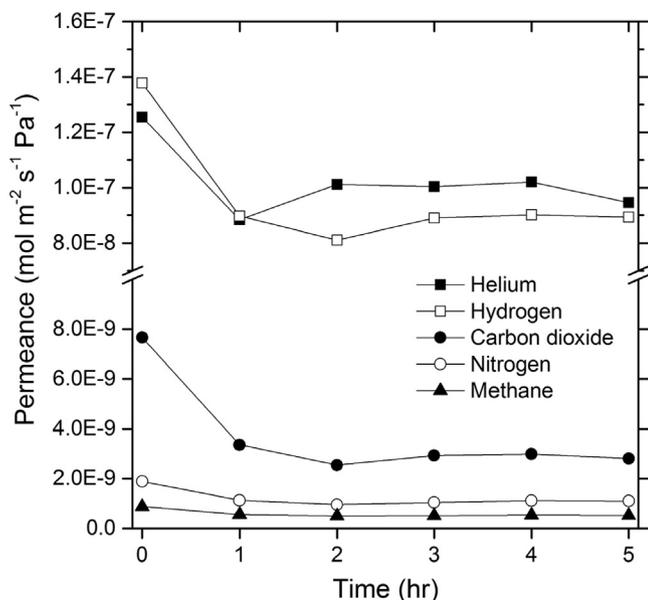


Fig. 5. Time course of permeance of a Zr-BTESE hybrid silica membrane measured at 200 °C with a transmembrane pressure of 2 bar after several hydrothermal treatment cycles at 200 °C.

so it is assumed that a steady state is achieved within two hours of hydrothermal treatment at 1 kPa and 200 °C. The permeance values after 5 h obtained during this in-situ treatment are in good agreement with the results from the 72 h static tests under WGS conditions at 200 °C (compare the results in Fig. 3, sample B200 with those in Fig. 5).

The lower permeances for the smaller gases after hydrothermal treatment at 200 °C of the Zr-BTESE membranes could be explained by two mechanisms. One mechanism is densification due to structural relaxation, which however is a slow process due to diffusion limitations. Such a process takes 50 h or more [20]. However, in our work a decline in permeance to a stable value was observed within a relatively short time of 2 h. Besides, if structural relaxation and consequently changes in pore morphology during hydrothermal treatments is responsible for the observed change in gas permeation, it is expected that this also might occur for the undoped BTESE membranes, which was not observed, as can be seen from the permeation results of sample Z and Z300 (see Fig. 2). A second mechanism, that can lead to lower permeances, is the partial blocking of the pores by water. For validation of this latter mechanism the interaction of water with BTESE and Zr-BTESE was studied in detail as will be discussed in the next section.

3.4. Water desorption behavior

In order to gain a better insight in the reason for the changes in gas permeances for Zr-BTESE membranes after a hydrothermal treatment at 200 or 300 °C, the dehydration behavior of calcined, hydrothermally treated, powdered samples was studied by thermogravimetric analysis (TGA), see Fig. 6. The TGA curve of the BTESE-derived hybrid silica powder depicts a steep decline in mass below 100 °C. In this region the loosely bound water desorbs. Above 100 °C no further weight loss was observed.

On the other hand, the Zr-BTESE hybrid silica powder continuously shows a mass decline above 100 °C what could be caused by the loss of water which is adsorbed on the zirconia. Numerous studies [21–24] show that there is a very strong chemisorption of water onto zirconia. Desorption of water from zirconia is there-

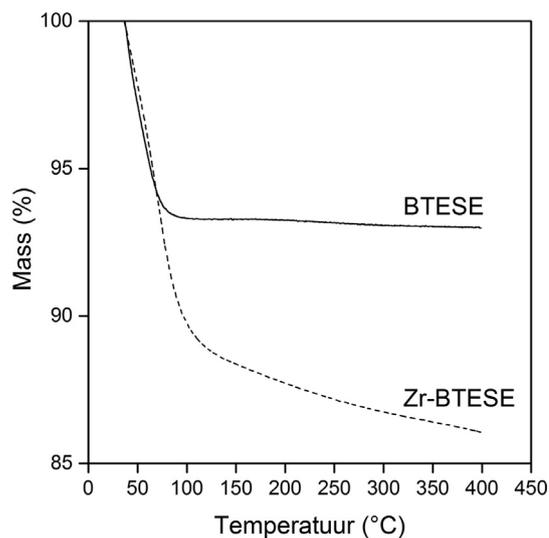


Fig. 6. TGA curve of drying calcined BTESE and Zr-BTESE membrane material with a heating rate of 5 °C/min under nitrogen.

fore not complete at temperatures below 400 °C. In catalysis, silica-zirconia mixed oxides are used as an acid catalyst [25], in which the nature of the acidity of the catalyst can be tuned by the silica-zirconia ratio. It is shown by Garcia-Sancho et al. [26] that Brønsted acid sites can be generated in Zr-doped MCM-41 by a treatment in steam at 315 °C. Qi et al. [11] observed an increase in H₂/CO₂ selectivity during steam treatment of Nb-BTESE derived hybrid silica membranes at 200 °C. In this work of Qi et al. it was hypothesized that the high acidity of these sites results in a decrease in affinity for CO₂ and hence in a lower CO₂ permeance than for undoped BTESE derived hybrid silica membranes. Boffa et al. [27] stated that the lower CO₂ permeance in niobia doped silica membranes is due to the strong adsorption of CO₂ on the surface of the membranes. This behavior was claimed because of the fact that, by means of FTIR analysis, CO₂ adsorption on hydroxyl groups was observed. However, in that work CO₂ adsorption was also observed for undoped (pure) silica membranes.

Based on literature, it can be assumed that the presence of Brønsted acid sites on zirconia, formed during hydrothermal treatment of Zr-BTESE derived hybrid silica membranes, could be responsible for the deviating CO₂ permeance, when compared with the non-hydrothermally treated Zr-BTESE hybrid silica membranes. Though, a sufficient high temperature is necessary for creating these Brønsted acid sites. If the permeance and permselectivity results of the Z100 membrane are compared with Z200 and Z300 membranes, it can be seen that for the Z100 membrane no significant increase in H₂/CO₂ permselectivity is observed (see Table 2). It seems that the formation of Brønsted sites by water vapor only occurs at higher temperatures. The lower permeances for the Z100 membrane, compared with an undoped BTESE derived hybrid silica membrane (B100), can therefore purely be ascribed to the chemisorption of water in the pores of the membrane. For the Z200 and Z300 membranes the creation of Brønsted sites leads to a further decrease in CO₂ permeance, which is beneficial for a better H₂/CO₂ selectivity.

4. Conclusions

An effective, straightforward hydrothermal stability test was developed to analyze and compare the hydrothermal stability of different ceramic membranes. Also under these circumstances, pure silica (TEOS) membranes were not able to retain their

separation performance after this hydrothermal treatment, while BTESE and Zr-BTESE hybrid silica membranes did not show any selectivity loss.

Hydrothermal stability tests under a simulated WGS mixture of BTESE derived hybrid silica membranes displayed no significant changes in permeance and selectivity after a hydrothermal treatment at 300 °C. Increasing this temperature to 400 °C results in an increase in the methane permeance showing that, after this hydrothermal treatment, degradation starts to occur in BTESE-derived hybrid silica membranes. A similar trend was observed for the Zr-BTESE hybrid silica membranes.

Remarkably, a large reduction in carbon dioxide permeance is observed for Zr-BTESE hybrid silica membranes, after hydrothermal treatment at 200 and 300 °C, resulting in a significant increase of the H₂/CO₂ permselectivity from 12 to 35. The Brønsted-acidic nature of Zr/Si mixed oxides is regarded to be the main cause of this relative strong decrease in CO₂ permeance.

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