

# Zeolite Membranes for Hydrogen and Water Separation under Harsh Conditions

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To increase the efficiency of power plants, coal can be processed by integrated gasification combined cycle (IGCC) to H<sub>2</sub> and CO<sub>2</sub>. To minimize efficiency losses during gas separation, nanoporous membranes can be used advantageously for the separation of H<sub>2</sub> and CO<sub>2</sub>. This process has to be carried out under hydrothermal process conditions (40 to 400 °C, 1 to 40 bar and 0.4 to 35 % water). The same membranes can be used for water separation applications like in the Fischer-Tropsch synthesis (FTS).

Sodalite (SOD) exhibits pore sizes in the range of the kinetic diameter of H<sub>2</sub> (0.29 nm), but is normally not hydrothermal stable. To increase the hydrothermal stability, the sodalite (H-SOD) was doped with sulphur (S-SOD). S-SOD is stable at 800 °C in dry atmosphere and 270 °C in 30 % water and approximately 40 bar. S-SOD membranes were synthesized on tubular alumina supports via a seeding procedure and subsequent hydrothermal synthesis. Crack free intergrown SOD-layers were found for membranes prepared with low concentrated seeding solutions. These membranes show a thickness of about 2 µm. Single gas permeation measurements gave a H<sub>2</sub>/CO<sub>2</sub>-permselectivity of 12 at room temperature for the best membranes. Variations of the seeding process lead to stable membranes up to at least 300 °C. These membranes showed an increasing selectivity with increasing temperature.

## 1. Introduction

After the world energy outlook of 2012, the global energy demand will be growing by more than one-third until 2035 (IEA, 2012). China, India and the Middle East account for 60 % of the growth, but there will be a pronounced shift towards gas and renewables. The main energy source will remain fossil fuels (coal, oil and natural gas), which produce about 60 % of the entire produced energy in Germany, at the moment. Therefore the emissions of greenhouse gases like CO<sub>2</sub> will also further increase. Currently about one third of the global CO<sub>2</sub>-emissions are products of power plants. To decrease the CO<sub>2</sub>-emissions of future power plants, the coal can be gasified to H<sub>2</sub> and CO<sub>2</sub> before the combustion (IGCC) (Pruscek et al., 1995). Subsequently, the hydrogen has to be separated from CO<sub>2</sub> and after that is burned in a gas turbine. The produced water vapour is fed to a steam turbine-generator. So the CO<sub>2</sub> emissions decrease and the efficiency increases in comparison to conventional fossil power plants. To decrease the very high efficiency losses of gas separation with methods like gas scrubbing or adsorption, nanoporous membranes can be used for H<sub>2</sub> and CO<sub>2</sub> separation. This separation has to be carried out under hydrothermal process conditions (40 °C – 400 °C, 1 bar – 40 bar and 0.4 % – 35 % water) (Czyperek et al. 2009, 2010). Further energetic process optimizations are expected by using catalytic membrane reactors (CMR). Development of CMR for Autothermal Reforming, Water Gas Shift reaction (WGS) (Brunetti et al., 2012), Fischer-Tropsch-Synthesis (FTS) and Oxidative Coupling requires membranes of high thermal and hydrothermal stability (Khassin et al., 2005).

Zeolites are crystalline tectosilicates with defined nanopores, which can be deposited as a thin layer on porous substrates. These zeolite membranes are cheaper than palladium (Lattner et al., 2002) or platinum membranes, but of course more expensive than polymeric membranes (Pinnau et al., 2011). In comparison to that, zeolite membranes show the big advantage of thermal and hydrothermal stability,

which is essentially for the former mentioned applications. Sodalite (SOD) exhibits pore sizes of 0.29 nm, which lies in the range of the kinetic molecule diameter of hydrogen. CO<sub>2</sub> should be too big for passing through the small pores of the sodalite framework. Therefore sodalite membranes are candidates for the molesieving H<sub>2</sub>/CO<sub>2</sub>-separation (size exclusion).

First sodalite powders were synthesized and their hydrothermal behavior was tested. The classical easy synthesized hydroxysodalite (H-SOD) is not hydrothermal stable. So the sodalite was doped with sulfur to enhance the stability (Günther et al., 2011). This so called S-SOD is stable at 10 bar – 57 bar, 25 % - 30 % water and 270 °C and allowed the production of crack free membranes.

## 2. Experimental

S-SOD membranes were synthesized on the inside of tubular alumina supports (250 mm length) via a seeding procedure and a subsequent hydrothermal synthesis. Different seeding materials were tested. H-SOD, TMA-AISi-SOD (Münzer et al., 2007) and S-SOD were used for support seeding. These zeolite powders were prepared by classical hydrothermal synthesis. The H-SOD synthesis solution was prepared by mixing an aluminate and a silicate solution in a polypropylene bottle (Khajavi et al., 2007, 2010). S-SOD was synthesized with an additional third solution of sodium sulphide nonahydrate in water. The S-SOD membrane synthesis was carried out under the same conditions like the S-SOD powder synthesis, with the one exception that tubular supports with a seeding layer are present. The purity of the powders was characterized with XRD measurements on a Bruker D8 Advance. The membranes were measured via single gas permeation measurements. The crystal sizes and morphology of the membranes were determined by scanning electron microscopy (SEM) and by field emission scanning electron microscopy (FE-SEM) with the help of a JEOL JSM-T200 and a Zeiss Ultra 55 plus with an EDAX Trident XM4 sensor for energy dispersive X-ray (EDX) spectroscopy.

### 2.1 H-SOD synthesis

The aluminate solution was prepared by mixing 33.5 g sodium hydroxide and 2.5 g sodium aluminate in 70 g deionised water. The silicate solution was prepared by dissolving 30 g sodium hydroxide and 6.5 g sodium metasilicate pentahydrate in 70 g water. The silicate solution was added to the aluminate solution and the resulting mixture was stirred for one hour to produce a defined altered solution. This solution was poured in an autoclave and synthesized for 20 h at 80 °C. The resulting powder was washed with deionised water and dried.

### 2.2 TMA-AISi-SOD synthesis

7 g tetramethylammonium hydroxide (TMAOH) solution 25 wt% in water, and 1.5 g aluminum isopropylate were slowly added to 5 g water. The solution was first stirred for 30 min at room temperature and then stirred for 1 h at 60 °C. In a second solution were 30 g tetramethylammonium hydroxide (TMAOH) solution 25 wt% in water and 7.5 g tetramethyl orthosilicate (TMOS) mixed with 7 g water. This solution was stirred for 1 h at room temperature. Subsequently the second solution was dropwise added to the first solution under intense stirring. The resulting solution was stirred at room temperature overnight. The alcohols of the clear solution were removed via distillation. The remaining solution was filled in an autoclave and synthesized at 170 °C for 4 days.

### 2.3 S-SOD synthesis

The aluminate and silicate solutions were prepared identical to the H-SOD synthesis. In a third solution 55 g sodium sulphide nonahydrate were dissolved in 90 g water. Then the silicate and the sulphide solution were added to the aluminate solution one after another. The solution changed the colour to orange after adding the sulphide solution. The resulting mixture was stirred for one hour to produce a defined altered solution and synthesized for 20 h at 80 °C in an autoclave.

## 3. Results and Discussion

Tubes were chosen because of the higher membrane area and the higher pressure stability, but the characterization is more difficult than with plates. The tubes have to be broken for SEM images and EDX measurements. The sulphur sodalite (S-SOD) is based on silica and alumina, therefore sodalite can easily intergrow with alumina supports and also the support can be accounted as a feed material for the zeolite building. The amount of zeolite which crystallizes during synthesis increases by the factor of 1.5 to 2, when an alumina support is present. In contrast to that, the presence of S-SOD seeding crystals only leads to a small increasing of the yield in the range of 10 – 20 %. 100 nm  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports are thermal and hydrothermal stable in the range up to 300 °C and were therefore selected for this application.

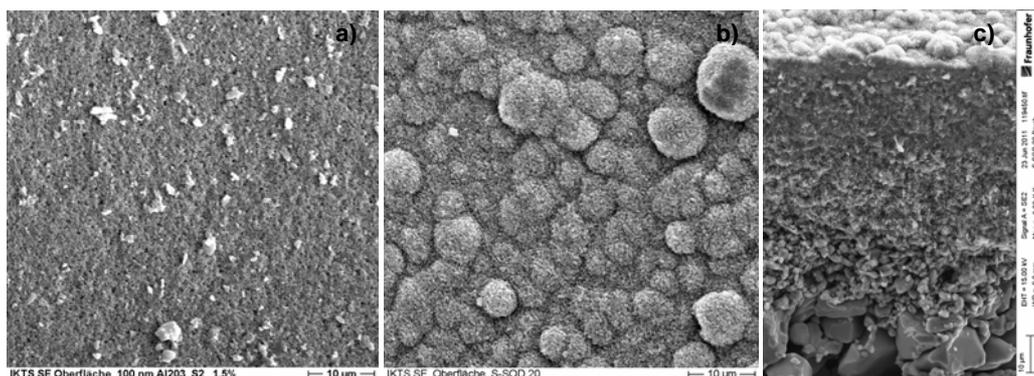


Figure 1: SEM images of a) H-SOD seeding; b) surface and c) cross-section of H-SOD seeding + S-SOD synthesis.

The H-SOD used for the seeding exhibits a Si/Al ratio of approximately 1 (Table 1). All synthesized S-SOD membranes (Table 2) show the same Si/Al ratio as H-SOD. The main difference between S-SOD and H-SOD is the additional sulphur content of 4.5 wt% and the correlating higher sodium content. This behavior confirms the addition of sodium sulfide to the zeolite framework. It is comparable to the difference between the structure of hydroxy sodalite  $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ,  $0 < n \leq 4$  and ultramarine  $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{S}_x$ ,  $0 \leq x \leq 5$ . The synthesized S-SOD contains certain amounts of water and hydroxy groups, but shows no coloring. Ultramarine gets calcinated at 850 °C (Kowalak et al., 1995) to attain the blue color and cannot be hydrogenated again. This behavior was not found for S-SOD. So the structure of S-SOD has to be something between hydroxy sodalite and ultramarine. The powders were characterized with XRD measurements, which exhibit the same pattern as known from the literature for hydroxy sodalite crystals (Khajavi et al., 2010). The additional sulphur in the S-SOD shifts the spectrum only slightly.

Supports seeded with an H-SOD slurry seeding show particles of different sizes at the surface (Figure 1 a). No seeding layers or clear crystals are visible. The support becomes more infiltrated with increasing concentration of the slurry. This leads to a densification of the top zone of the support. After an S-SOD synthesis on top of the H-SOD seeding, an uneven membrane layer with an average of 2  $\mu\text{m}$  thickness was found (Figure 1 b and c). The membrane was build of sodalite aggregates with a cauliflower structure. This membrane type shows a permselectivity from hydrogen to carbon dioxide of 12 and from hydrogen to sulphur hexafluoride of 24 at room temperature (black line with balls in Figure 2). The hydrogen flux is about  $0.09 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$  and the flux of sulphur hexafluoride about  $0.004 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ . Hence, defects in the layer have to exist. Furthermore H-SOD is not thermal stable, so the whole membrane is not stable at higher measuring temperatures e.g. 150 °C or 300 °C. The fluxes increased to a not measurable level and the selectivity dropped. Therefore the seeding was changed.

For the synthesis of TMA-AlSi-SOD, the tetramethylammonium group is used as a structure directing template. Nano-seeds of this composition could be synthesized and used for the seeding of the membrane. The seeding layer shows plate structures (Figure 3 a), but these structures decompose during

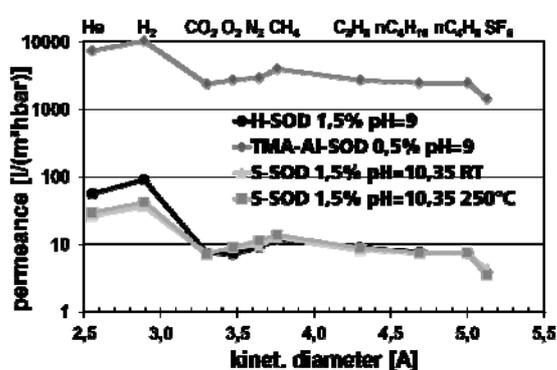


Figure 2: Single gas permeances of S-SOD membranes with different seedings.

Table 1: Results of the EDX analysis of the H-SOD seeding.

	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
wt%	18	37	45
mol%	20	26	54

Table 2: Results of the EDX analysis of an S-SOD membrane.

	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	S
wt%	23	33	39.5	4.5
mol%	25	22	44	9

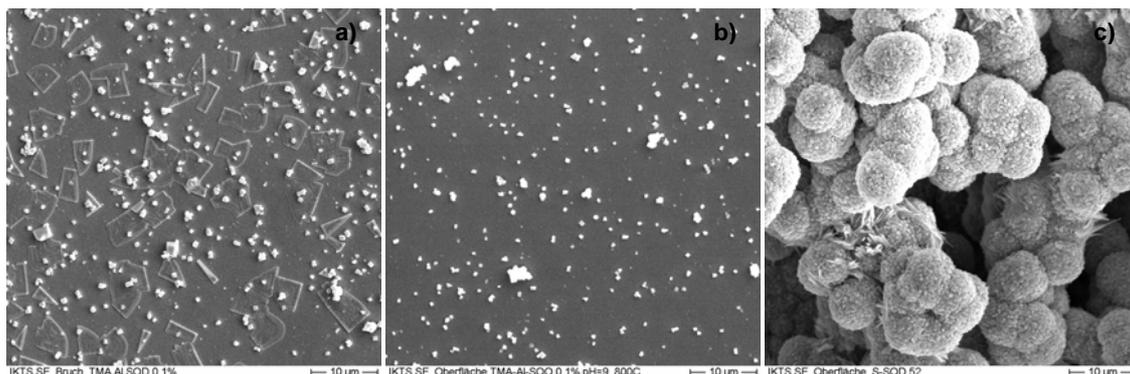


Figure 3: SEM images of a) TMA-AISi-SOD seeding; b) TMA-Al-SOD seeding after detemplating; c) TMA-AISi-SOD seeding + S-SOD synthesis.

detemplating at 800 °C (Figure 3 b). The detemplating is necessary, because the template blocks the cages of SOD and no permeation through the SOD network is possible. But with detemplating the structure of the seeding layer changes and after the following S-SOD synthesis, only an uneven membrane layer with holes and impurities could be achieved (Figure 3 c). These membranes show very high fluxes and a low selectivity (at best Knudsen selectivity), which is a consequence of the holes (dark grey line with diamonds in Figure 2). The hydrogen flux is with  $10.3 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$  about 100 times higher than for the H-SOD seeding, but the permselectivity from hydrogen to carbon dioxide is only 4.5. Also no measuring at higher temperatures is possible, because the already high fluxes increase further. Hence, this seeding type is no option for the membrane synthesis and the seeding had to be changed for a second time.

The S-SOD slurry seeding is comparable to the H-SOD seeding (Figure 1 a). Only small particles of different sizes are visible at the surface of the support. With an S-SOD synthesis on top of the S-SOD seeding, a closed membrane layer of smaller crystals with about 2 µm thickness was achieved (Figure 4). Only some bigger cauliflower-like agglomerates were present. This type of membrane shows fluxes in the range of the membranes seeded with H-SOD e.g. for hydrogen of  $0.035 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$  (light grey line with triangles in Figure 2). The permselectivity from hydrogen to carbon dioxide is with about 5 a little bit higher than with the TMA-AISi-SOD seeded membranes, but smaller than for the H-SOD seeded ones. But the membranes seeded with S-SOD were able to be measured at 300 °C (medium-grey line with squares in Figure 2). The fluxes remain in the same range like at room temperature and the permselectivity from hydrogen to carbon dioxide increased a little bit to 5.9. The thermal stability at 300 °C is essential for potential high temperature membrane applications like power plants, WGS and FTS. Therefore only the S-SOD seeding can be used for further membrane synthesis. The hydrogen flux und the permselectivity need further increasing to develop a competitive membrane. The bigger agglomerates have to be reduced or eliminated to increase the membrane performance. This could be achieved by the using of smaller seeding crystals or an optimization of the grinding process for the slurry production. By EDX Analysis up to 1.5 % zirconia impurities were found in the membranes and the support. This measuring method is not

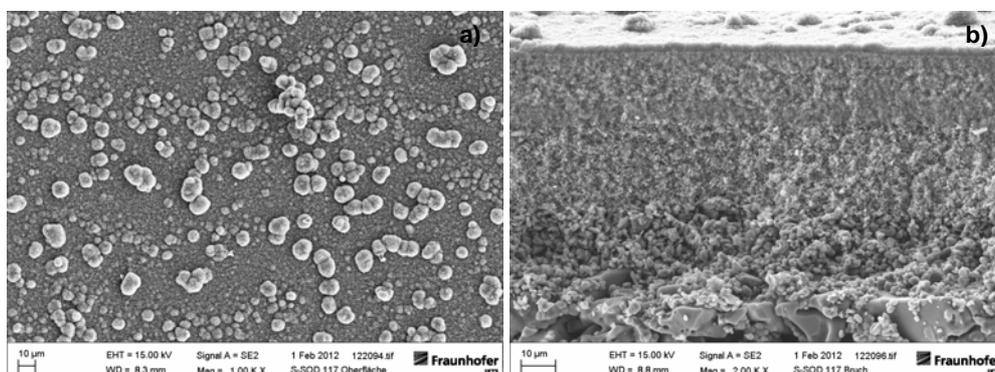


Figure 4: SEM images of a) surface and b) cross-section of S-SOD seeding + S-SOD synthesis.

very accurate, but the basic behavior can be recognized. The zirconia was introduced by grinding with zirconia balls. It is considered foreign to the zeolite membrane and resulting into defects. For this reason, next alumina grinding balls were tested. But a kind of agglomeration occurs, when alumina grinding balls are used for the grinding of S-SOD. Alumina is a part of the zeolite framework and is obviously a good reaction partner for the sodalite. For the support this is an advantage, because a good connection or growing together is possible. But for the grinding process, it is a big problem. So other kinds of grinding balls or grinding processes without balls have to be tested to achieve smaller seeding particles without impurities.

#### 4. Conclusions

The seeding procedure is essentially for the stability of the membrane. Only if the seeding is thermal stable, the whole membrane can be stable. H-SOD crystals, TMA-AISi-SOD nanoseeds and sulphur doped S-SOD crystals have been synthesized and used as seeding materials for membrane synthesis. S-SOD membranes have been successfully synthesized on top of the three different types of seeding. The membranes seeded on H-SOD show the highest achieved permselectivity from hydrogen to carbon dioxide of 12 until now. But the H-SOD seeding is not stable at higher temperatures. The TMA-AISi-SOD seeding decomposes during detemplating and no membrane layer with good separation properties could be prepared on top of this seeding. The S-SOD seeding with following S-SOD synthesis shows the most promising results. The membranes are thermal stable at least until 300 °C and the permselectivity from hydrogen to carbon dioxide increases a little bit from 5 to 5.9 at this higher temperature. Therefore only the S-SOD seeded membranes satisfy the requirement of a thermal and hydrothermal stable membrane for potential high temperature membrane applications like power plants, WGS and FTS. With further optimizations of the seeding procedure and the grinding process, an improved performance should be possible.

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