DOI: http://dx.doi.org/10.22104/ijhfc.2015.171

Iranian Journal of Hydrogen & Fuel Cell 4(2014) 209-214

Iranian Journal of Hydrogen & Fuel Cell

IJHFC

Journal homepage://ijhfc.irost.ir

Effect of dehydration temperature on the H_2 separation potential of hydroxy sodalite zeolite membranes

Mohammad Javad Vaezi[1] and Ali Akbar Babaluo[1,*]

[1]Nanostructure Material Research Center (NMRC), Sahand University of Technology, P.O.Box 51335-1996, Tabriz, Iran
Chemical Engineering Faculty, Sahand University of Technology, P.O.Box 51335-1996, Tabriz, Iran

Article Information

Article History:

Received:
12 November 2014
Received in revised form:
25 July 2015
Accepted:
26 July 2015

Keywords

Dehydration temperature
Hydrogen separation
Hydroxy sodalite
Zeolite membrane

Abstract

The main goal of this work was to synthesize and evaluate the effect of dehydration temperature on the potential application of hydroxy sodalite zeolite membrane. Hydroxy sodalite zeolite membranes were synthesized via direct hydrothermal method onto a tubular alumina support without seeding in a hot air oven. The synthesized membranes were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Permeation tests of H_2 and CO_2 were carried out in order to investige the applied dehydration temperature effect on the performance of the synthesized membranes. The performance of the synthesized membrane dehydrated at 100 ºC tended to high selectivity compared to the rest of the samples and the maximum separation factor (~21) was achieved with acceptable permeances about 3.8×10^{-8} and 1.8×10^{-9} $mol.m^{-2}.Pa^{-1}.s^{-1}$ for H_2 and CO_2, respectively. The low selectivities observed for two other synthesized membranes (dehydrated at 150 and 200 ºC)indicated the formation of defects during the dehydration of these membranes at high temperatures.

1. Introduction

Hydrogen is widely used in various industrial fields, such as chemical, oil refining and petrochemical industries, and is a clean energy source for the future. Among various hydrogen sources and production methods about 50% of world's hydrogen is produced from fossil fuels by means of steam reforming reactions and water electrolysis [1-3]. In addition to the production methods the separation and purification of hydrogen is very important because pure hydrogen is receiving increasing attention as a clean energy

*Corresponding author. Tel.: +984133458084; Fax: +984133458084.
E-mail address: a.babaluo@sut.ac.ir (a.a. babaluo)

source [4]. Considering that the production of hydrogen still results in the production of carbon dioxide [5], using effective methods for hydrogen purification is necessery. One of the novel methods for hydrogen purification is membrane technology. H_2 selective membranes provide an attractive alternative to PSA and cryogenic distillation as it is a more cost-effective H_2 purification method than both of these [6-8]. Dense Pd-based metallic, carbon molecular sieve (CMS), microporous amorphous silica or doped silica and zeolite membranes are also interesting research subjects to develop inorganic membranes for H_2 separation [8]. Among these, Pd-based membranes are more expensive and CMS membranes have a complex synthesizing procedure while zeolite membranes, as one of the inorganic membranes with molecular sieve-like properties, have a relatively high gas permeance and high stability even at higher temperatures and corrosive atmospheres [9]. Due to the same size of zeolites pores, these materials have long been considered as excellent candidates for separation and purification of gases [10].

Only a few studies on H_2 separation using zeolite membranes have been reported [11-13]. Sodalite with 6 membered rings (pore diameter = 2.8 Å), as shown in Fig.1, has been introduced as a high potential zeolite membrane for H_2 separation and molecular modeling studies on sodalite as one of the zeolites, and confirmed the high potential of this type of zeolite membranes for hydrogen separation [14-17].

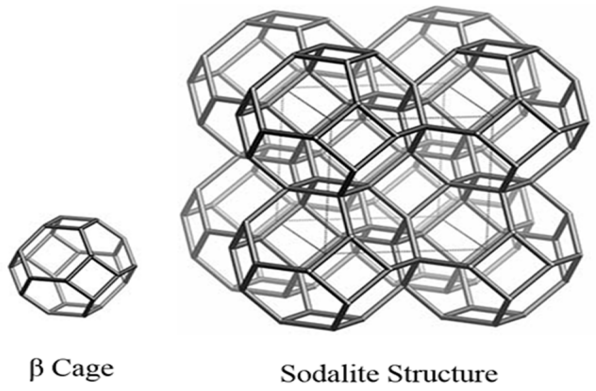

Figure 1. Sodalite β cage and its structure [17].

However, Julbe et al. [18] and Lee et al. [19] experimentally obtained low performance for the sodalite membranes in hydrogen separation. This difference between the experimental and modeling results may be related to the formation of non-zeolite pores in the thermal treatment step. This step is used to remove water molecules that block the pores of the sodalite membrane. Despite the high potential of sodalite for H_2 separation, only a few studies have reported on the thermal stability of a sodalite structure and its effect on the separation performance of this membrane.

Zeng et al. [14] studied the thermal stability of three kinds of sodalite (low, high and pure silica sodalite) at high temperatures and investigeted their performance for hydrogen separation. They reported that low silica sodalite (Si/Al=1) is stable up to ~250 ºC. Thermal gravimetry analysis of the different types of sodalite was also investigated and brief weight loss results were reported as presented in Table 1. Also, Khajavi et al. [20] reported that no change occurred in the crystalline structure of low silica sodalite after drying at different temperatures in the range of 30-250 ºC after comparing their XRD patterns. In addition, their TGA-DTA analyses results revealed about a 7 wt% loss in the weight of low silica sodalite due to release of its water molecules at 150 and 350 ºC. So, it can be claimed that the main weight loss of low silica sodalite is in the temperature range of 100-200 ºC. This temperature range in the dehydration step may be very important for low silica sodalite. But to the best of our knowledge, few studies on the drying temperature effect on the gas separation performance of sodalite membranes have been reported in the literarature.

Table 1. Temperature range of different types of sodalite with the maximum derivation weight (MDW) [14].

	Low Silica Sodalite (Si/Al=1)	High Silica Sodallite (Si/Al=5)	Pure Silica Sodalite (Si/Al→ ∞)
Temperature range of MDW	100-200 ºC	150-250 ºC	400-500 ºC

The main aim of this study was to synthesize

hydroxy sodalite membranes on the outer surface of a homemade tubular ceramic support via the hydrothermal method. The prepared membrane morphology and crystalinity were characterized by SEM and XRD analyses, respectively. The prepared membranes were dried at three different temperatures (100, 150 and 200 ºC) and the single gas permeation of H_2 and CO_2 through the prepared membranes was carried out to choose the best drying temperature to obtain high selective membrane.

2. Experimental

2.1. Membrane prepartion procedure

Homemade tubular α-alumina supports were prepared by the gel casting method (6 mm inner diameter, 12 mm outer diameter, 3 mm in thickness, average pore size 570 nm and average porosity of 47.2%) as described in our previous work [21]. Before applying the support for membrane synthesis, they were cleaned in acetone by an ultrasonic generator for 3 min and then dried at 70°C for 3 h. The solution for the synthesis of the membrane was obtained by mixing the appropriate two solutions, aluminate and silicate. The aluminate solution was prepared by dissolving sodium hydroxide (5.72 g, NaOH, Merck, > 99 %) and aluminum (0.14 g, Al, Merck,> 99 %) in deionized water (25 ml). Also, the silicate solution was prepared by mixing sodium hydroxide (4.87 g) and silica sol (2.75 ml, [SiOx(OH)4-2x]n, Merck, 27 wt.% SiO_2) in deionized water (22.7 ml). The aluminate solution was preheated to 50 ºC before adding to the silicate solution. The final mixture was stirred vigorously to reach a clear homogeneous solution. Finally, the synthesized solution molar ratio was $5SiO_2$:Al_2O_3:$50NaO_2$:$1000H_2O$. The prepared solution was carefully poured into a Teflon holder in a stainless steel autoclave without hitting the support, and then the autoclave was sealed. The synthesis was carried out at 90 °C for 12 h. After washing the synthesized membranes several times with deionized water to reach pH 7, they were dried at 100 (M1), 150 (M2) and 200 (M3) °C for 3 h with low heating and cooling rates (lower than 0.5 °C/min).

2.2. The prepared membrane characterization

XRD measurements were carried out on a Bruker D8 ADVANCE X'Pert diffractometer using CuKa (l=1.54 Å) radiation operating at 40 kV and 40 mA (Step Size = 0.05°(2θ)). SEM analysis was used to investigate the morphology and thickness of the prepared membrane. Before gas permeation measurements, the synthesized membranes were dried at 100, 150 and 200 °C for 3 h to dehydrate the sodalite membrane pores. The dehydrated membranes were placed into a stainless steel permeation cell and sealed with VITON gaskets. Single gas permeation was measured by a soap-film flow meter at room temperature under the different pressures.

3. Results and Discussion

Fig. 2 shows the XRD pattern of the synthesized membrane. XRD reflections of the synthesized membrane were correlated to the reference XRD of hydroxy sodalite [22], indicating the successful formation of hydroxy sodalite on the support surface. Also, the XRD pattern of the synthesized membrane contains some other extra peaks corresponding to α-alumina support and zeolite impurities or formation of new crystals rather than sodalite.

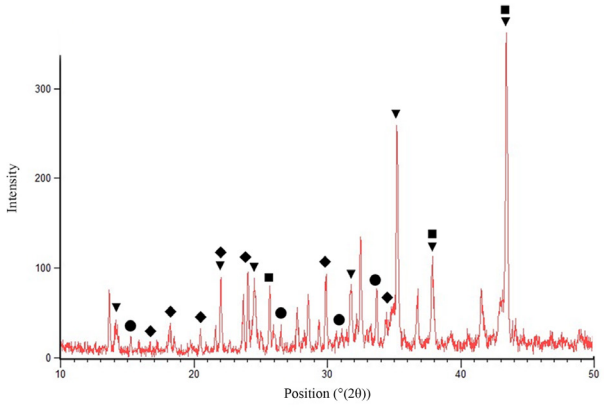

Figure 2. XRD pattern of α-alumina supported hydroxy sodalite membrane:
(▼)sodalite, (■)α-alumina, (♦)Na-A and (●)Na-X.

The SEM images of a surface and cross section of the synthesized hydroxy sodalite membrane are shown in Fig.3. According to the cross section image of the synthesized membrane, the average membrane thickness of hydroxy sodalite layer was 25 µm. Also, as is visible from the surface image, zeolite crystals were found to be well grown and a continuous integrated membrane layer was formed, which coincides with the XRD pattern.

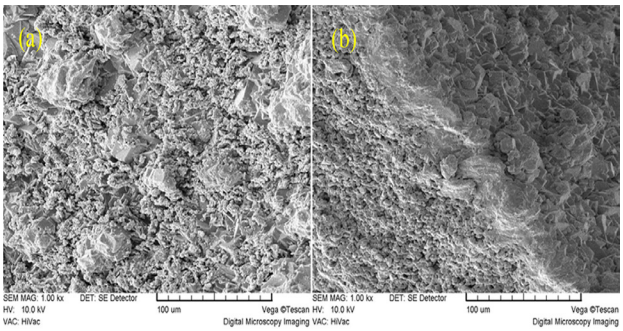

Figure 3. Top view (a) and cross-section (b) of the synthesized hydroxy sodalite membrane.

The synthesized membrane quality was evaluated by single gas permeation measurement without dehydration (removing water from its structure). This measurement found that before the drying step the membrane had no permeance for nitrogen, confirming the preparation of a defect-free membrane.

To investigate the effect of dehydration temperature on the performance of the synthesized membranes, the sodalite membranes performance was evaluated after drying at 100, 150 and 200 ºC. Fig. 4 gives the permeances of H_2 and CO_2 as single gases for the membrane dried at 100 ºC (M1). As can be seen, the permeance of gases increases by increasing mean pressure which may be due to the existance of non-zeolitic pores and zeolite impurities like Na-A and Na-X. It is known that permeance of CO_2 and other gases with a kinetic diameter larger than the pore diameter of zeolites with six-membered rings is not possible. Therefore, the non-zero permeance of CO_2 molecules can be attributed to non-zeolitic pores created through the grain boundaries of the sodalite layer and the existance of 8, 10 or 12 membered rings in the membrane's structure.

Another observation that can be made by comparing the gases permeance data (Fig. 4), is that the slope of CO_2 permeance-pressure curve is higher than that of H_2. As mentioned earlier, the permeance of CO_2 is related to nanometric non-zeolitic pores. So by considering the Knudsen selectivity of H_2/CO_2 (4.7), it was found that the non-zeolitic pores contribution in H_2 permeance was less than 30% and H_2 transport through the zeolitic pores of membrane is dominant. Therefore, the effect of mean pressure on the H_2 permeance is lower than CO_2 permeance. On the other hand, the existance of 8, 10 or 12 membered rings related to zeolites like Na-A and Na-X results in polar molecule adsorption at high pressures hence their permeance increases.

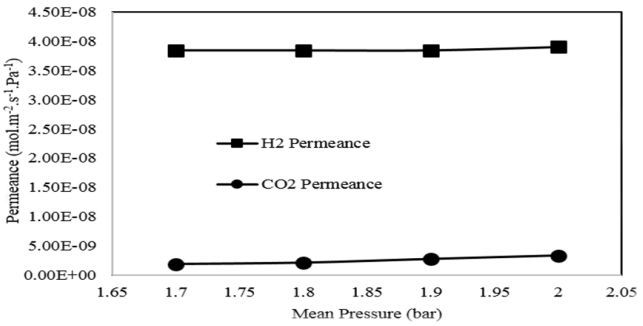

Figure 4. Permeance of H_2 and CO_2 through the membrane M1 (dried at 100 ºC) at room temperature.

In addition, to further demonstrate the effect of dehydration temperature on the separation performance of sodalite zeolite membranes, the ideal selectivities of the prepared membranes dried at 100 (M1), 150 (M2) and 200 (M3) ºC were determined as a function of mean pressure as shown in Fig. 5. As can be seen, the H_2/CO_2 ideal selectivity of M1 is more than 10 which remarkably exceeds the Knudsen separation factor (~4.6) even at high pressures.

The most obvious observation is that the performance of the membrane dried at 100 ºC is much higher than those of the other ones. A considerable decrease in the membranes performance is noted when the drying temperature increases from 100 ºC to 150 ºC. By increasing the drying temperature from 150 ºC

to 200 ºC, the selectivity does not change so sharply and reached the non-size selective Kundsen-like mass transport. These results can be attributed mainly to the thermal behavier of the prepared membranes at different dehydration temperatures.

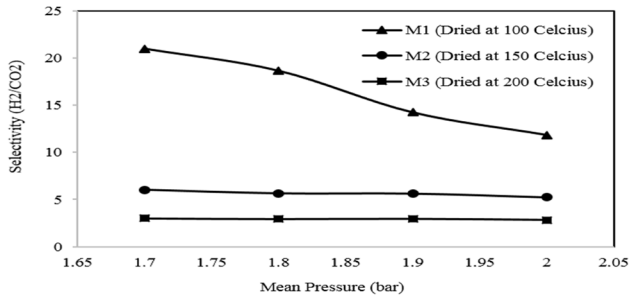

Figure 5. Ideal selectivity of H_2 over CO_2 at room temperature for M1 (dried at 100 ºC), M2 (dried at 150 ºC) and M3 (dried at 200 ºC) membranes.

Further explanation would be that the maximum derivation weight of hydroxy sodalite with low silica (Si/Al=1) is in the range of 100-200 ºC with the maximum point at 150 ºC [14]. Also, the TGA-DTA analysis of the synthesized hydroxy sodalite powder in Fig. 6 shows that the maximum derivation weight of the synthesized zeolite is in the range of 115-125 ºC. So that when heating the membrane up to this temperature and beyond some defects in the microstructure of sodalite membrane may occur which cause low selectivity in the separation of small gas molecules. The maximum derivation of weight during the removal of water from the sodalite cages can be the main reason for the creation of some defects in the final membrane structure.

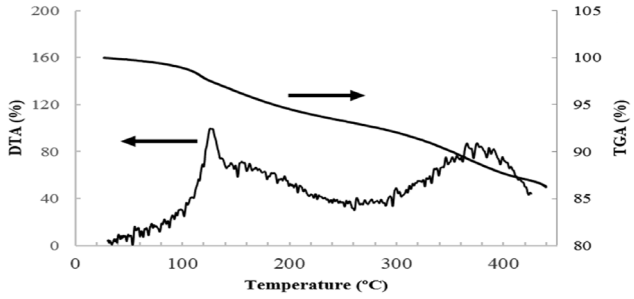

Figure 6. TGA-DTA analysis of the synthesized hydroxy sodalite powder.

4. Conclusions

A hydroxy sodalite membrane with high performance for hydrogen separation was prepared on a tubular α-Al_2O_3 support. The effect of dehydration temperature (100-200 ºC) was investigated on the performance of sodalite membranes for the first time. The observed negative effect of increasing the dehydration temperature suggests that the synthesized sodalite membrane should be dried at temperatures lower than 150 ºC and near to 100 ºC to avoid the maximum derivation weight. The obtained results indicated that the membrane dehydrated at 100 ºC is a high potential membrane for the sepration of H_2 from other gases like CO_2.

5. References

[1] Kanezashi M. and Asaeda M., "Hydrogen permeation characteristics and stability of Ni-doped silica membranes in steam at high temperature", J. Membr. Sci., 2006, 271: 86.

[2] Akamatsu K., Ohta Y., Sugawara T., Kanno N., Tonokura K., Hattori T. and Nakao S., "Stable high-purity hydrogen production by dehydrogenation of cyclohexane using a membrane reactor with neither carrier gas nor sweep gas", J. Membr. Sci., 2009, 330: 1.

[3] Itoh N., Watanabe S., Kawasoe K., Sato T., and Tsuji T., "A membrane reactor for hydrogen storage and transport system using cyclohexane–methylcyclohexane mixtures", Des., 2008, 234: 261.

[4] Koutsonikolas D., Kaldis S., Zaspalis V.T. and Sakellaropoulos G.P., "Potential application of a microporous silica membrane reactor for cyclohexane dehydrogenation", Int. J. Hydrogen Energy, 2012, 37: 16302.

[5] Rahimpour M.R. and Bayat M., "Production

of ultrapure hydrogen via utilizing fluidization concept from coupling of methanol and benzene synthesis in a hydrogen-permselective membrane reactor", Int. J. Hydrogen Energy, 2011, 36: 6616.

[6] Sircar S. and Golden T.C., "Purification of Hydrogen by Pressure Swing Adsorption", Sep. Sci. Technol., 2000, No.5, 35: 667.

[7] Huang C.P. and Rassi A., "Analyses of One-Step Liquid Hydrogen Production from Methane and Landfill Gas", J. Power Sources, 2007, No.2, 173: 950.

[8] Li Y., Liang F., Bux H., Yang W. and Caro J., "Zeolitic imidazolate framework ZIF-7 based molecular sieve membrane for hydrogen separation", J. Membr. Sci., 2010, 354: 48.

[9] Nishiyama N., Yamaguchi M., Katayama T., Hirota Y., Miyamoto M., Egashira Y., Ueyama K., Nakanishi K., Ohta T., Mizusawa A. and Satoh T., "Hydrogen-permeable membranes composed of zeolite nano-blocks", J. Membr. Sci., 2007, 306: 349.

[10] Ackley M., "Application of natural zeolites in the purification and separation of gases", Micropor. Mesopor. Mater., 2003, 61: 25.

[11] Lai R. and Gavalas G.R., "ZSM-5 membrane synthesis with organic-free mixtures", Micropor. Mesopor. Mater., 2000, 38: 239.

[12] Masuda T.F.T, Fukumoto N., Kitayama M., Mukai S.R., Hashimoto K. and Tanaka T., "Modification of pore size of MFI-type zeolite by catalytic cracking of silane and application to preparation of H_2-separating zeolite membrane", Micropor. Mesopor. Mater., 2001, 48: 239.

[13] Sebastian J.C.V., Lin Z., Rocha J., Tellez C. and Santamaria J., "Synthesis, characterization, and separation properties of Sn and Ti-silicate umbite membranes", Chem. Mater., 2006, 18: 2472.

[14] Zheng Z., Guliants V.V. and Misture S., "Sodalites as ultramicroporous frameworks for hydrogen separation at elevated temperatures : thermal stability, template removal , and hydrogen accessibility", J. Porous Mater., 2009, 16: 343.

[15] Van den Berg A.W.C, Bromley S.T., Flikkema E. and Jansen J.C., "Effect of cation distribution on self-diffusion of molecular hydrogen in $Na_3Al_3Si_3O_{12}$ sodalite: A molecular dynamics study", J. Chem. Phys., 2004, 121: 10209.

[16] Nabavi M.S., Mohammadi T. and Kazemimoghadam M., "Hydrothermal synthesis of hydroxy sodalite zeolite membrane: Separation of H_2/CH_4", Ceram. Int., 2014, 40: 5889.

[17] Baerlocher Ch., McCusker L.B. and Olson D.H., 6th ed., Atlas of Zeolite Framework Types, Published on behalf of the Stucture Commision of the International Zeolite Association, 2007.

[18] Julbe A., Motuzas J., Cazevielle F., Volle G. and Guizard C., "Synthesis of sodalite/αAl_2O_3 composite membranes by microwave heating", Sep. Purif. Technol., 2003, 32: 139.

[19] Lee S.R., Son Y.H., Julbe A. and Choy J.H., "Vacuum seeding and secondary growth route to sodalite membrane", Thin Solid Films, 2006, 495: 92.

[20] Khajavi Sh., Sartipi S., Gascon J., Jansen J.C. and Kapteijn F., "Thermostability of hydroxy sodalite in view of membrane applications", Micropor. Mesopor. Mater., 2010, 132: 510.

[21] Babaluo A.A. and Kokabi M., "Manufacture of porous support systems of membranes by in-situ polymerisation", Iran Polym. J., 2002, 15: No.3.

[22] Treacy M.M.J. and Higgins J.B., 4th ed., Collection of Simulated XRD Powder Patterns for Zeolites, Published on behalf of the Stucture Commision of the International Zeolite Association, 2001.