



## Performance of PDMS/SSZ-13 mixed matrix membrane for CO<sub>2</sub>/N<sub>2</sub> separation

D. D. Athayde<sup>a,b\*</sup>, A. C. Takahashi<sup>a</sup>, G. L. A. Silva<sup>a</sup>, I. L. de Almeida<sup>a</sup>, J. S. A. Paes<sup>a</sup>, N. D. S. Mohallem<sup>c</sup>, A. M. A. Silva<sup>b</sup>  
<sup>a</sup>Department of Chemical Engineering, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil  
<sup>b</sup>Department of Mechanical Engineering, Universidade de Brasília, Brasília, Brazil  
<sup>c</sup>Department of Chemistry, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil  
\*ddathayde@gmail.com

### Abstract

Flue gases emitted from many sources based on fossil fuels typically present high concentrations of CO<sub>2</sub> and N<sub>2</sub>, with the carbon dioxide representing one of the main components responsible for greenhouse gas emissions. In the current global context, in which intense climatic changes are already underway, the decarbonization of energy systems is listed as one of the main challenges for future engineers and researchers [1]. In order to achieve this goal, an efficient separation of CO<sub>2</sub> and N<sub>2</sub> is required for posterior use of CO<sub>2</sub> capture technologies. Among the available technologies, the membrane separation process is already listed as a potential alternative for CO<sub>2</sub>/N<sub>2</sub> separation, since it is a simple and scalable process [2]. Despite the current performance limitations of the initial materials used for membrane manufacture, the concept of mixed matrix membrane has shown in recent years the capacity for great improvement when an inorganic filler, such as microporous zeolite, is immersed in a polymeric matrix [3].

In this study, the goal is to assess the improvements on the separation performance of mixed matrix membranes produced by incorporating SSZ-13 zeolite into a polydimethylsiloxane (PDMS) polymer using different SSZ-13 particles with varying concentrations. The SSZ-13 zeolite with pore windows of 0.38 nm was produced hydrothermal synthesis based on already reported synthesis [4]. The reagents (tetraethylorthosilicate – TEOS, NaOH, Al(OH)<sub>3</sub>, and N,N,N-trimethyl-1-adamantylammonium hydroxide – TMAOH) were mixed for 1h and placed in an oven at 160 °C for periods varying within 1-4 days. The obtained white powder was washed and heat treated at 600 °C for 6 hours with 5 °C/min. The calcined SSZ-13 powder was then manually mixed with PDMS precursor (Sylgard™ 184) using SSZ-13 mass concentrations varying within 5-15% and stirred. Then, the mixture was placed in a Teflon sheet and spread using a cast knife. Finally, the cast PDMS/SSZ-13 film was left in an oven at 80 °C for 90 minutes. The final thickness of the film was within 200-300 μm. The CO<sub>2</sub>/N<sub>2</sub> separation performance was explored using pure gases based on an already published setup [5]. The permeability (*P*, in barrer) and ideal selectivity ( $\alpha$ ) were calculated using Eq. (1) and Eq. (2), respectively [5].

$$P = \frac{dp_2}{dt} \times \frac{V_s}{A \times p_1} \times \frac{T_{stp}}{T_{room}} \times \frac{1}{p_{stp}} \times L \quad (1)$$

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \quad (2)$$

where  $p_2$  and  $p_1$  are permeate and feed pressure, respectively,  $t$  is time,  $V_s$  is the permeate stream volume (equal to 8.94 cm<sup>3</sup>),  $A$  is the membrane area (1.63 cm<sup>2</sup>),  $T_{stp}$  is 273.15 K,  $T_{room}$  is the room temperature during the tests,  $p_{stp}$  is the standard pressure (76 cmHg),  $L$  is the membrane thickness, and  $P_{CO_2}$  and  $P_{N_2}$  are the CO<sub>2</sub> and N<sub>2</sub> permeabilities.

The mixed matrix PDMS/SSZ-13 membranes obtained in this study revealed that the use of SSZ-13 zeolites obtained with only 1 day hydrothermal synthesis led to poor particle dispersion of the particles within the polymeric matrix, as shown for the sample 1d05% in Fig. 1. As for the membranes produced with SSZ-13 zeolites with 4 day hydrothermal synthesis, the dispersion was adequate with homogeneous distribution of the SSZ-13 particles, forming a translucent film (Fig. 1) with increasing opacity as the SSZ-13 concentration increased. The different dispersion among the samples is due to the SSZ-13 particle properties (different sizes and morphologies of SSZ-13 particles), and only the samples 4d05%, 4d10%, 4d15% led to reproducible samples with appropriate mechanical stability for performance tests.

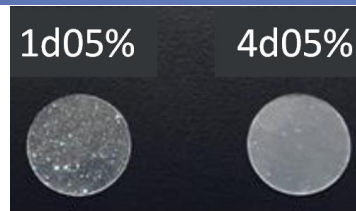


Fig. 1 – Picture of the obtained PDMS/SSZ-13 membranes. The sample 1d05% has 5% of SSZ-13 particles produced with 1 day hydrothermal synthesis, and the sample 4d05% has 5% of SSZ-13 particles produced with 4 days hydrothermal synthesis.

The permeability tests revealed that the incorporation of SSZ-13 zeolites, which are microporous materials with higher selectivity for the CO<sub>2</sub>/N<sub>2</sub> separation when compared to the PDMS, resulted in considerable impacts on the CO<sub>2</sub> permeability whilst no significant changes on the N<sub>2</sub> permeability were noticed. For instance, the sample 4d05% had a 25.7% superior permeability when compared with PDMS sample (an increase from 1910 to 2402 Barrer), whereas the N<sub>2</sub> permeability kept considerably similar to the PDMS (around 220 Barrer). This behavior resulted in higher CO<sub>2</sub>/N<sub>2</sub> selectivity, reaching values as high as 10.89 for the 4d05% samples. Even though the SSZ-13 zeolite incorporation provided improvements on the separation performance, membranes with concentrations of SSZ-13 higher than 5% showed lower values of CO<sub>2</sub> permeability and ideal selectivity than the PDMS membrane.

The performance of the samples showed that the incorporation of SSZ-13 zeolite was positive for CO<sub>2</sub>/N<sub>2</sub> separation for SSZ-13 concentrations up to 5%, while highest concentrations were detrimental to the separation performance reaching selectivities as low as 7.4. This behavior was already reported as a challenge for development of zeolite-polymer mixed matrix membranes [6], and the hypothesis is that the high concentration of zeolite (>5%) within the polymer matrix caused rigidification of the polymer and affected the pathways that CO<sub>2</sub> diffuses through the mixed matrix membrane. This result was also correlated to results from thermogravimetric tests, which agreed well with previous studies [6].

Despite the many challenges on development of novel membrane materials, a simple and effective method of incorporating SSZ-13 zeolites into PDMS, a polymer simple to synthesize and to cast, showed the potential of mixed matrix membranes for improving both the permeability and selectivity of gas separation membranes, which is paramount for further development and engineering of membrane-based separation processes.

## References

- [1] National Academies of Engineering. "Chemical engineering: challenges and opportunities in the 21<sup>st</sup> century", [Online]. Available at: <https://www.nationalacademies.org/our-work/chemical-engineering-challenges-and-opportunities-in-the-21st-century>.
- [2] Kamble, A.R., C. M. Patel, Z. V. P. Murthy. "A review on the recent advances in mixed matrix membranes for gas separation processes", *Renew. Sust. Energ. Rev.*, 145, 111062 (2021).
- [3] Bastani, D, N. Esmali, M. Asadollahi. "Polymeric mixed matrix membranes containing zeolites as filler for gas separation applications: a review", *J. Ind. Eng. Chem.*, 19, 375-393 (2013).
- [4] Zeng, L., Z. Yu, Z. Sun, Y. Han, Y. Xu, J. Wu, Z. Liang, Z. Wang, "Fast synthesis of SSZ-13 zeolite by steam-assisted crystallization method", *Microporous Mesoporous Mater.*, 293, 109789 (2020).
- [5] Paraense, M. O., T. H. R. da Cunha, A. S. Ferlauto, K. C. S. Figueiredo. "Monolayer and bilayer graphene on polydimethylsiloxane as a composite membrane for gas-barrier applications", *J. Appl. Polym. Sci.*, 134, 45521 (2017).
- [6] Ahmad, M. Z., V. Martin-Gil, T. Supinkova, P. Lambert, R. Castron-Muñoz, P. Hrabanek, M. Kocirik, V. Fila, "Novel MMM using CO<sub>2</sub> selective SSZ-16 and high-performance 6FDA-polyimide for CO<sub>2</sub>/CH<sub>4</sub> separation", *Sep. Purif. Technol.*, 254, 117582 (2021).