Separation and Capture of CO₂ through A Zeolitic Membrane †

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Abstract: This paper presents the development and evaluation of a technology for CO_2 separation and capture from a mixture of post-combustion gases through a zeolitic membrane. A silicalite-1 membrane was hydrothermally synthesized to selectively separate CO_2 from a CO_2/N_2 mixture and permeation tests were performed on the mixture and the simple gases. The composition and morphology of the silicalite-1 crystals were confirmed by XRD and SEM/EDS. The recovered CO_2 was used as raw material for its transformation into inorganic media like carbonates.

Keywords: CO_2 separation; zeolitic membrane; carbonation; silicalite-1

1. Introduction

One of the actions to achieve a reduction in CO_2 emissions is the introduction of combustion gas separation techniques, through using membrane technology [1]. Zeolites have a significantly large, uniform porosity system, excellent thermal and chemical stability, so they are particularly promising as membranes capable of separating gases at industrial level [2], like CO_2 from combustion gases [3]. The gas separation properties in membranes depend on: the material (permeability, separation factors), the structure of the membrane and the thickness, the membrane wall and the design of the module and the system [4]. After separation and capture, CO_2 can be used partially for commercial purposes or it can be stored, isolating it from the atmosphere thereby reducing its concentration in it [5]. Carbonation involves the formation of solid carbonates, a reaction between carbon dioxide and alkaline/alkaline earth oxides [6]. Considering these aspects, this study presents the development and evaluation of CO_2 separation technology from a mixture of post-combustion gases through a zeolitic membrane and its capture of CO_2 by carbonation.

2. Materials and Methods

A tubular silicalite-1 membrane was hydrothermally synthesized, then subjected to permeation and gas separation studies of a CO_2/N_2 mixture performing in a stainless steel permeation module in the 25 to 200 °C range temperature and 30 psi pressure of the feed gases: the CO_2/N_2 mixture was fed in 1:1 volumetric ratio. The composition of the gas flow was analyzed by means of a gas chromatograph (Agilent 6890) with an HP-PLOTQ column connected in line, with helium as the carrier gas. The synthesis gel was prepared with Degussa 200 aerosil, as a silica source, 1M tetrapropylammonium hydroxide (TPAOH) Aldrich, as structure directing agent and deionized water. The gel was allowed to mature for 72 h with constant agitation. The synthesis of the silicalite-1

layer was carried out on a commercial monotubular ceramic support of γ-alumina (Pall). The 15 cm long tubular support was waterproofed at both ends (1.5 cm each end). The synthesis of the silicalite-1 layer was carried out on a commercial monotubular ceramic support of γ-alumina (Pall). The 15 cm long tubular support was waterproofed at both ends (1.5 cm each end). The synthesis was carried out at 170 °C and autogenous pressure, for 72 h. This procedure was repeated 4 times over to ensure formation of an homogenous, defect-free silicalite-1 layer on the inner wall of the support. The membrane was characterized by elemental analysis through a SEM/EDS equipment (Carl Zeiss, model supra PV55, fitted with an Oxford detector for Energy Dispersive Spectroscopy Analysis (EDS)) and by X-ray diffraction (XRD) (in Philips X'Pert equipment). The recovered CO_2 was captured by inorganic media promoting the formation of carbonates. The CO_2 was fed to a reactor with $Sr(OH)_2$, $Ba(OH)_2$ or $Mg(NO_3)_2$ 0.06M alkaline solutions at room temperature and normal atmospheric pressure (≈25–30 °C and 585 mmHg Mexico City, Mexico), with the CO_2 fed at a flow of 15.17 mL/min. A $Na(OH)$ 0.1 M solution was added to the $Mg(NO_3)_2$ solution in order to obtain $Mg(OH)_2$, for further CO_2 carbonation reactions. After reaction the solids were filtered out, then dried at 80 °C, and characterized by elemental analysis, as stated.

3. Results and Discussion

3.1. Characterization of membrane

Figure 1a shows a membrane cross section SEM micrograph where the growth of the zeolite crystals can be observed on the inner support surface used in the synthesis; energy dispersive spectroscopy analysis is also presented (Figure 1b) which yielded a composition: 58 wt% oxygen and 38.01 wt% silicon, as major elements. Figure 1c shows the XRD diffraction pattern of the synthesized zeolite crystals compared to the zeolite MFI reference standard, obtained from the Zeolite Structures Database [7]. In the XRD diffraction pattern, the similarity in the peaks intensity and their location in the 2θ angle can be observed.

Element	Weight%
C K	3.60
O K	58.00
Si K	38.01
K K	0.39
Totals	100.00

(**a**) (**b**) (**c**)
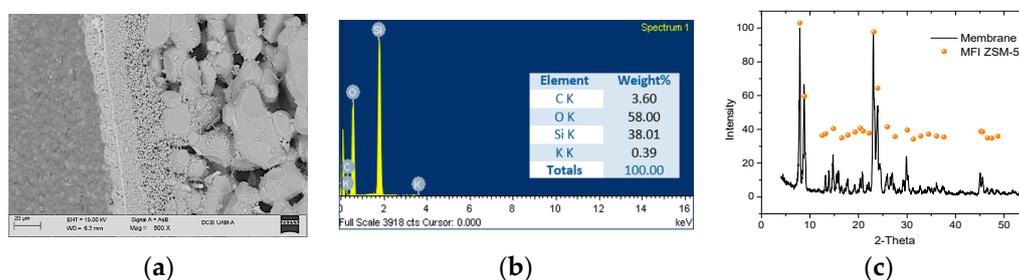
Figure 1. (**a**) cross section of the mesoporous support, formed by three layers and a zeolite film, (**b**) EDS membrane analysis, (**c**) MFI membrane XRD diffraction pattern.

3.2. Results of permeation and gases separation

The permeation results of the simple gases N_2 and CO_2 in the membrane show a decreasing trend when temperature increases, being in the 1.6176×10^{-7} to 2.8354×10^{-7} mol m^{-2}s^{-1} Pa^{-1} range for N_2 and 1.7451×10^{-7} to 2.8954×10^{-7} mol m^{-2}s^{-1}Pa^{-1} for CO_2. In the case of the CO_2/N_2 mixture, the permeation also decreases as a function of temperature; however, the permeation values are greater than that of the simple gases, namely, from 4.4404×10^{-7} to 6.7358×10^{-7} mol m^{-2}s^{-1}Pa^{-1} (Figure 1).

According to Bakker, et al. (1997), the temperature dependence of the flows in steady state, in the range of −83 to 407 °C through a silicalite-1 membrane, can be described using two diffusion mechanisms. Under conditions where a considerable amount of gas is adsorbed, diffusion is carried out by mass transport in an adsorbed site (surface diffusion) while at high temperatures, diffusion is described by gas transport diffusion [8] since there is virtually no adsorption.

The results of the gases separation show a maximum separation factor (SF) of 2.1 at 25 °C, that decreased with increasing temperature, as can be seen in Table 1.
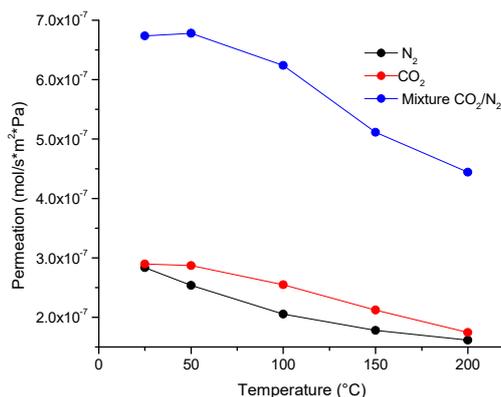
Figure 1. Permeation of simple gases CO_2 and N_2 and CO_2/N_2 mixture.

Table 1. Results of gas separation factor.

Temperature (°C)	SF
25	2.1003
50	1.9162
100	1.6681
150	1.4075
200	1.2273

The separation factor is the result of the composition of the permeate flow and not of the amount of flow, therefore, considering a higher molecular adsorption at low temperatures and the size of the molecules of CO_2 (3.3 Å) and N_2 (3.64 Å) it is presumed that the membrane performed a slightly selective separation of CO_2 over the entire temperature range, due to the CO_2 molecule smaller size with respect to that of N_2.

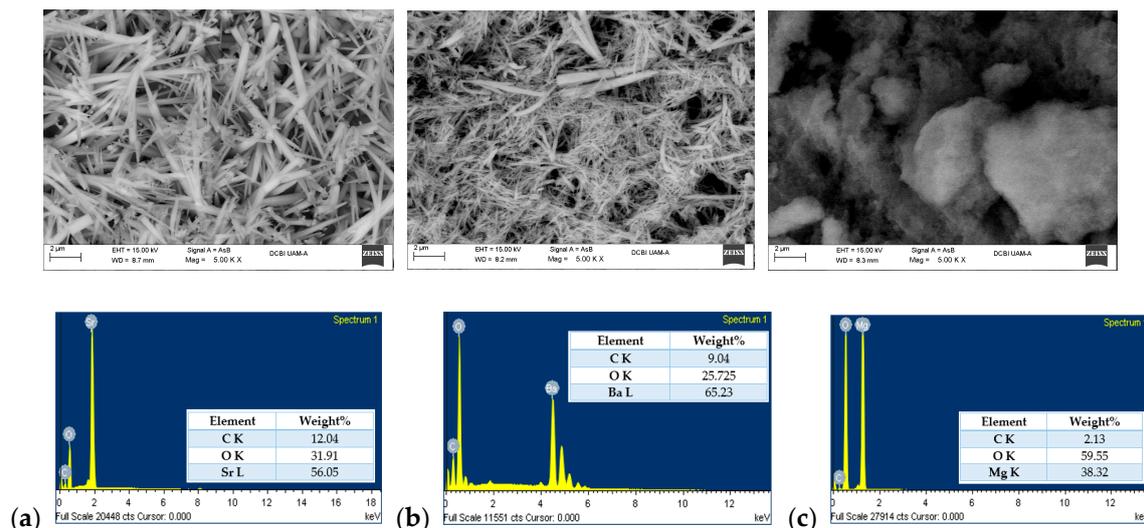*3.3. Solids Recovered from Carbonation Reactions*

The dry weight of the solids recovered in the carbonation reactions was recorded in order to perform a mass balance and obtain the conversion percentage of each reaction with respect to the initial concentration of the alkaline solutions and with the CO_2 flow fed. The results on conversion percentage are shown in **Error! Reference source not found.**

Table 2. Conversion percentage in carbonation reactions.

Reaction Time (Minutes)	Conversion Percentage		
	$Sr(OH)_2$	$Ba(OH)_2$	$Mg(NO_3)_2$
20	40.22	85.09	57.60
30	26.06	69.07	29.07
40	20.11	66.50	17.67

3.4. Characterization of Solids Recovered after Carbonation Reactions

The Figure 3 shows the morphology of the solids recovered in the carbonation reactions with the different alkaline solutions as well as the elemental analysis carried out that shows the presence of carbon in the solids.

Figure 3. Micrographs and EDS analysis of the solids recovered after the carbonation reactions with (**a**) $Sr(OH)_2$; (**b**) $Ba(OH)_2$; (**c**) $Mg(NO_3)_2$.

4. Conclusions

The permeation studies allowed the determination of the surface diffusion mechanism of gases through the membrane. A slight selectivity of CO_2 with respect to N_2 was obtained after gases separation with a factor up to 2.1 at 25 °C. Considering the mechanism of diffusion, the characteristics of the membrane, as well as the separation factor, it is concluded that the synthesis resulted in a membrane capable of separating CO_2 from a CO_2/N_2 mixture under the study conditions, although it is possible to obtain more favorable results by chemically modifying the basic surface properties of the membrane.

The CO_2 capture system shows that it is possible to obtain other compounds starting with CO_2, recovering it as carbonates, and the characterization of these compounds showed that they can be used as raw material in another process.

Author Contributions: M.G.-A. and M.T.-R. conceived of and designed the experiments and analyzed the data, D.S.-N. performed the experiments and V.M.-A. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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