

## Single Gas Permeation on $\gamma$ -Alumina Ceramic Support

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### Abstract

This study examines the characterization (SEM-EDXA observation, BET measurement) and gas transport through a commercial tubular alumina mesoporous (20 and 500 Å) support. Single gas permeation of helium (He), hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) was measured at a temperature of 450°C and feed pressures between 0.85 up to 1.0 bar. Observation of the permeance of the alumina support revealed that the transport of the gases under these conditions is governed by Knudsen diffusion. Selectivity of 2.7 was obtained for He/N<sub>2</sub> at 1 bar. The selectivity obtained is comparable to the theoretical Knudsen value (2.65) for He/N<sub>2</sub>.

**Keywords:** Alumina support; Gas permeation; Gas selectivity; Knudsen diffusion

### Introduction

Applications of inorganic membranes continue to receive tremendous growth in the last three decades due to their improved permeances and thermal stabilities. In many cases, membrane technology has been efficiently applied in the industrial sectors in order to replace the conventional energy-demanding as well as environmentally polluting separation systems [1]. Inorganic membranes have been successfully applied for carbon dioxide separation [2], hydrogen separation [3], high-purity water and recovery of toxic or valuable components from industrial effluents [4]. Membranes can be classified into organic and inorganic systems. The organic ones are further divided into biological and polymeric constituents, while the inorganic membranes can be divided into metallic and ceramic (porous and non-porous) membranes [3]. In recent time, membranes were fabricated from polymeric materials but these are exposed to chemical attack and cannot withstand high temperature. It is for these reasons that inorganic membrane technology is receiving increasing attention. Inorganic membranes are commonly made from ceramic, metal oxide or sintered metal, palladium metal, zeolite among others [3].

Gas transport through porous ceramic membranes depends on pore diameter [5]. According to the International Union of Pure and Applied Chemistry (IUPAC) definition; macro pores with pore diameter >500 Å, where basically viscous flow and Knudsen diffusion occur; mesopores with pore diameter between 20 and 500 Å, where basically Knudsen diffusion is the dominant; and micro pores with pore diameter <20 Å, where molecular sieving is expected [5]. The so-called Knudsen number is used to differentiate between viscous and Knudsen flow which is written as [5,6]:

$$K_n = \frac{\lambda}{d_p} \quad (1)$$

Where,  $\lambda$  is the mean free path of gas molecules, and  $d_p$  is the pore diameter.

Basically, the mean free path is the average distance travelled by the molecule between collisions. Therefore, mean free path is expressed as [6]:

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P} \quad (2)$$

Where, R is the gas constant (8.314 J.K<sup>-1</sup>.mol<sup>-1</sup>), T is the temperature (K), d is the diameter (m), N<sub>A</sub> is the Avogadro's number (mol), and P is the pressure (Pa).

Viscous flow is determined if the mean free path is smaller than the pore diameter, the flow characteristics are determined primarily by collisions among the molecules and can be written as [3,5,6]:

$$P_v = \left( \frac{\epsilon r_p^2 P_{av} \Delta P}{8\pi\mu RTL} \right) \quad (3)$$

Where, P<sub>v</sub> is the viscous permeance (mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>),  $\epsilon$  is the porosity of the membrane, r<sub>p</sub> is the mean pore radius (m), P<sub>av</sub> = P<sub>1</sub> + P<sub>2</sub> / 2 is the average pressure (Pa),  $\Delta P$  is the pressure drop across the membrane (Pa),  $\mu$  is the viscosity (Pas), and L is the thickness of the membrane (m).

Knudsen diffusion occurs if the mean free path is effectively larger than the pore diameter. The separation is based on molecular weight [3,5,6]. Thus, Knudsen permeance states that the permeation flux is proportional to the inverse square root of the molecular weight of the gas and temperature which can subsequently be written as [6]:

$$P_{kn} = \frac{\epsilon 8r_p \Delta P}{3\tau L (2\pi RTM)^{0.5}} \quad (4)$$

Where, P<sub>kn</sub> is the Knudsen permeance (mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>),  $\tau$  is the tortuosity and M is the molecular weight of the diffusing gas (g/mol).

However, if the mean free path of the gas molecule is equal to the pore diameter, then; the flow mechanism is governed by the combination of both mechanisms (i.e., Equations 3 and 4) which is written as:

$$P_t = \frac{\epsilon}{\tau L} \left[ \frac{r_p^2 (P_{av}) \Delta P}{8\mu RT} + \frac{8r_p \Delta P}{3(2\pi RTM)^{0.5}} \right] \quad (5)$$

Where P<sub>t</sub> is the total permeance (mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>).

In this study, a commercially  $\gamma$ -alumina support was characterized and single gas permeation and selectivity was carried out at feed pressures between 0.85 up to 1.0 bar and a temperature of 450°C in order to elucidate their respective gas transport mechanism.

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## Experimental

A commercial tubular gamma alumina support supplied by Ceramiques Techniques et Industrielles (CTI SA) France was employed in this study. The gamma alumina support was mesoporous (20 and 500 Å) consisting of 7 and 10 mm internal and outer diameter respectively. The symmetric alumina support consisted of a permeable length of 348 mm (Figure 1) and a porosity of 45%. The gases used were helium (He), hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>). Table 1 shows the detailed characteristics of the gases.

The experimental set-up consisted of a membrane reactor, gas delivery system for pure gases, a permeate and retentate exit, a flow meter and K-type thermocouples fixed on the reactor (Figure 2). However, prior to permeation experiments the reactor and all connections were tested for leaks by means of a soap solution. The permeation tests involved passing the gas into the shell-side and directed to permeate across the alumina support at different pressures and a temperature of 450°C. The shell is made from stainless steel material and has 28 mm I.D., 36 mm O.D., 395 mm long, 5 mm thick that can withstand high temperatures. The stainless steel shell was covered with heating tapes in order to maintain the heating of the reactor system. The two ends were removable for membrane replacement purpose. Gas tightness between the shells was maintained by graphite O-rings. Two graphite rings (one at each end) were used as sealing for the alumina tube ends which withstand high temperature as well as allowing for thermal expansion of the alumina membrane. The inlet pressure of the reactor were measured with highly accurate and versatile digital pressure measuring gauges (Keller Druckmesstechnik, Winterthur, Switzerland) with an accuracy of 0.1% factory setting at room temperature. The permeate was connected to a digital flow meter to measure the flow rates. The permeance was calculated as:

$$F=q/A\Delta P \quad (6)$$

Where, F is the Permeance (mol/m<sup>2</sup> s<sup>-1</sup> Pa<sup>-1</sup>), q is the molar flow (mol/sec), A is the surface area of the support (0.0062 m<sup>2</sup>),  $\Delta P$  is the pressure difference across the support (Pa).

Scanning electron microscopy (SEM) and energy diffraction X-ray analysis (EDXA) were obtained from Zeiss EVO LS10 electron microscope. Figure 3 depicts the cross-section SEM micrographs of the alumina support. Approximately 10  $\mu$ m thick alumina layer of highly intergrown alumina crystals was observed. Gas permeation

Gas	Kinetic Diameter (Å)	Molecular Weight (g/mol)
He	2.6	4
H <sub>2</sub>	2.89	2
N <sub>2</sub>	3.64	28
CO <sub>2</sub>	3.3	44

Table 1: Gas kinetic diameter and molecular weight.



Figure 1: Pictorial view of tubular gamma alumina support.

result reveals that the alumina support is defect free. Figure 4 depicts the EDXA result of the alumina support which clearly shows the Al<sub>2</sub>O<sub>3</sub> peaks.

Nitrogen adsorption-desorption isotherms were measured using an automated gas sorption analyzer (Quantachrome instrument version 3.0) at liquid nitrogen temperature (77 K). The specific surface area was evaluated using the Brunauer-Emmett-Teller (BET) method (Quantachrome instrument version 3.0). The pore diameter was also obtained using the Barret-Joyner-Halenda (BJH) method. He, H<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> with at least 99.999 (%v/v) purity was used for permeation characterization. Permeation tests were carried out at feed pressures between 0.85 up to 1.0 bar and a temperature of 450°C.

## Results and Discussion

### Membrane characterization

The N<sub>2</sub> adsorption-desorption isotherm of the alumina support was obtained. The BET surface area and the BJH pore size distribution methods of the alumina support are depicted in Figures 5 and 6. It can be seen in Figure 5 that the isotherm exhibits a drop in the desorption branch at  $P/P_0=0.5$  (dotted line). However, the meniscus curve is not closed, this could be as a result of contaminants in the material. The BET surface area of the alumina support is 0.364 m<sup>2</sup>/g. Figure 6 depicts the measurement of the pore-size distribution of the alumina support.

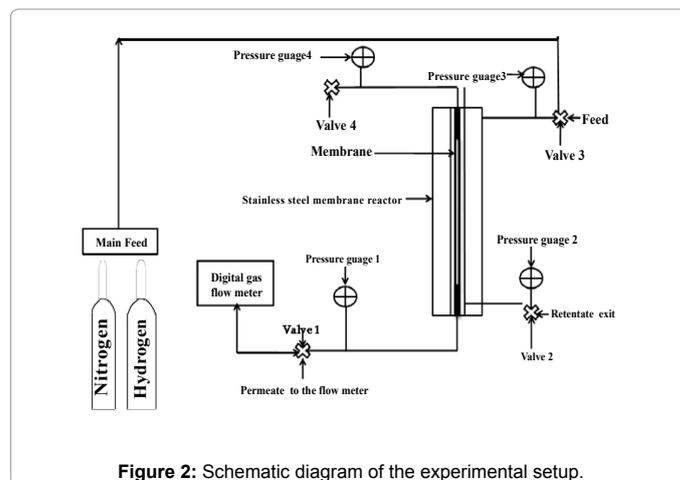


Figure 2: Schematic diagram of the experimental setup.

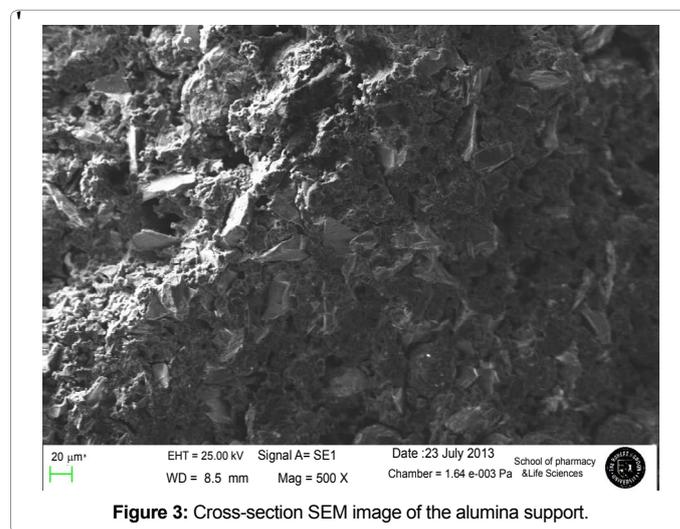


Figure 3: Cross-section SEM image of the alumina support.

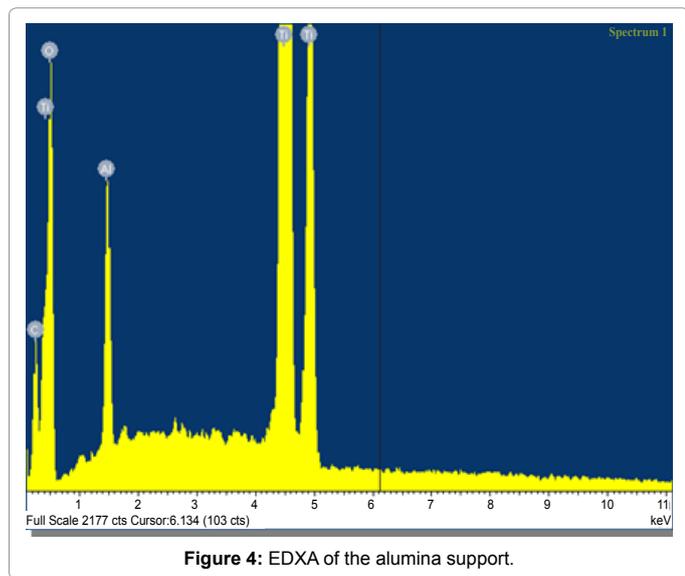


Figure 4: EDXA of the alumina support.

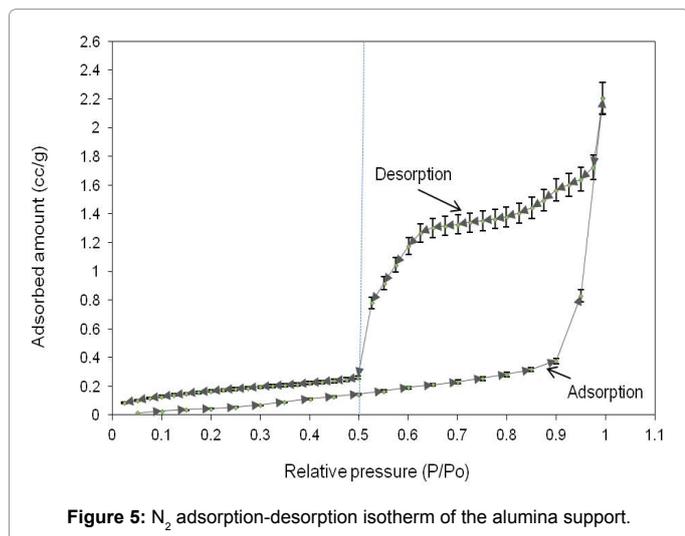


Figure 5:  $N_2$  adsorption-desorption isotherm of the alumina support.

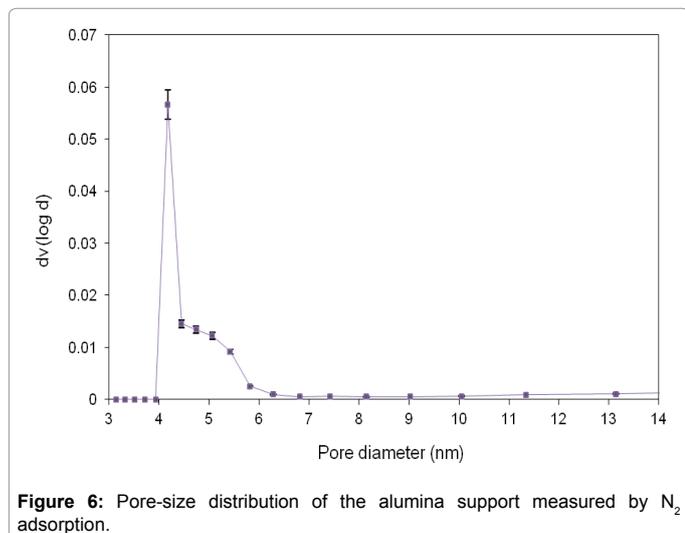


Figure 6: Pore-size distribution of the alumina support measured by  $N_2$  adsorption.

An average pore diameter of 4.171 nm is calculated from the pore-size distribution graph, and the pore volume is  $0.005 \text{ cm}^3/\text{g}$ .

The adsorption-desorption isotherm exhibits a characteristics of mesopores solids (especially ceramics) resulting in Type IV physisorption isotherm according to the IUPAC recommendations which revealed the presence of mesoporous ( $20 < \text{pore size} < 500 \text{ \AA}$ ) in the membrane undergoing capillary condensation and hysteresis during desorption [7-9].

### Gas permeation

The variation of He,  $H_2$ ,  $N_2$  and  $CO_2$  single gas permeances against permeation pressure across the alumina support was examined at  $450^\circ\text{C}$ . Figure 7 depicts gas permeances as a function of feed pressure across the alumina support. The permeances did not change with pressure increase which reveals that viscous flow contribution is not significant. From Equation (5); the first term can therefore be neglected

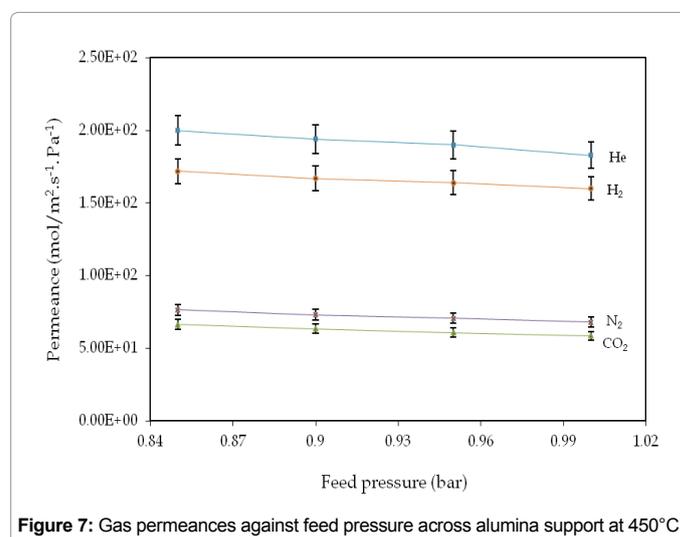


Figure 7: Gas permeances against feed pressure across alumina support at  $450^\circ\text{C}$ .

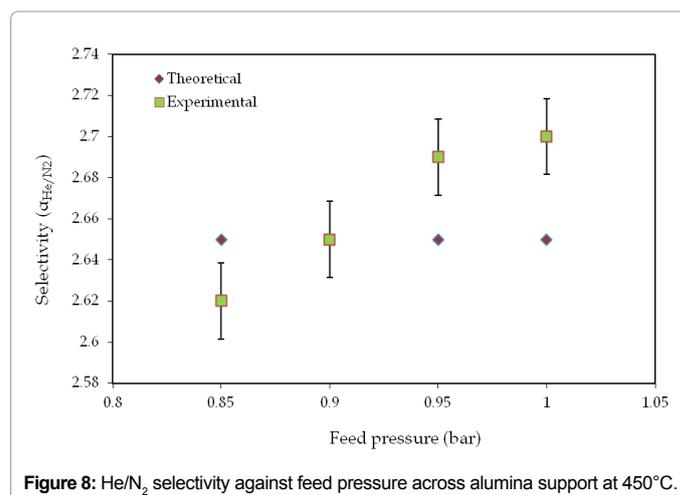


Figure 8: He/ $N_2$  selectivity against feed pressure across alumina support at  $450^\circ\text{C}$ .

Pressure (bar)	Permeances ( $\text{mol}/\text{m}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ )		Selectivity ( $\alpha_{He/N_2}$ )	
	He	$N_2$	Theoretical	Experimental
0.85	$2.00 \times 10^2$	$7.64 \times 10^1$	2.65	2.62
0.90	$1.94 \times 10^2$	$7.31 \times 10^1$	2.65	2.65
0.95	$1.90 \times 10^2$	$7.06 \times 10^1$	2.65	2.69
1.00	$1.83 \times 10^2$	$6.79 \times 10^1$	2.65	2.70

Table 2: He and  $N_2$  permeances and  $\alpha_{He/N_2}$  at  $450^\circ\text{C}$ .

from the governing transport through the alumina support, owing to the fact that Knudsen diffusion dominates the flow regime. The transport of the gases with respect to their kinetic diameter and molecular weight behaves differently. It can be seen on Figure 7 that, He and H<sub>2</sub> permeation followed their respective kinetic diameter, whereas, N<sub>2</sub> and CO<sub>2</sub> permeation followed their respective molecular weight. Figure 8 depicts He/N<sub>2</sub> selectivity against feed pressure at 450°C. It can be seen that He/N<sub>2</sub> selectivity of 2.7 (Table 2) at 1 bar is obtained. The selectivity obtained is comparable to the theoretical Knudsen value (2.65).

## Conclusions

The characterization (SEM-EDXA observation, BET measurement, permeation assessment) of a commercial tubular gamma alumina support was carried out. SEM result reveals that the alumina support is defect free. BET surface area, average pore diameter and the pore volume of the alumina support was also obtained (0.364 m<sup>2</sup>/g, 4.171 nm and 0.005 cm<sup>3</sup>/g). The adsorption-desorption isotherm exhibits a characteristics of mesopores solids. Single gas permeances were measured at feed pressures between 0.85 up to 1.0 bar and a temperature of 450°C. The permeances were influenced by Knudsen diffusion transport mechanism. He/N<sub>2</sub> selectivities obtained (2.7) were comparable to the theoretical Knudsen value (2.65).

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