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Structural Characteristic and Permeation of Gases through a Supported Silica Inorganic Ceramic Membrane

N. C Nwogu, M.N. Kajama, G. Osueke and E. Gobina

Abstract— The present paper describes the synthesis and hydrodynamic properties of a surface-modified ceramic membrane composed of a porous support which consists of gamma alumina and a titania wash-coat. Single gas permeation through the membranes was measured at 298 and 373K using H₂, N₂, Ar and CH₄. The membranes showed high separation factors of gases consistent with Knudsen diffusion mechanisms. Structural characteristic and pore size distribution of the porous and surface modified silica membrane was analysed with Liquid Nitrogen adsorption at 77K to obtain gas adsorption/desorption isotherm of membrane materials. Both surface area of the porous support and surface-modified silica membrane was determined using Brunauer-Emmett-Teller (BET) model to reproducible isotherms while the pore diameter of both membranes was determined using Barrette-Joyner-Halenda (BJH) curve. The adsorption/desorption curve for the surface-modified silica ceramic membrane showed a type IV/V isotherm which indicates a mesoporous makeup. This surface-modified membrane, therefore, displayed high thermal stability and high permeance. Further results obtained from the experiments conducted have helped explain the effect of dissimilarity in the mass-transfer on the gas permeation through the hybrid ceramic membranes.

Key words— Ceramic membrane, Gas permeance, Knudsen transport & selectivity

I. INTRODUCTION

THE separation of gases by selective transport through inorganic ceramic membranes is a vibrant and fast growing field in membrane technology [1] [2] [3]. In membrane-based gas separation process, components are separated from their mixtures by their difference in

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permeation through the membranes. A number of benefits, including low capital and operational costs, lesser energy requirements and ease of operation are offered by membrane separation [4] [5] [6]. As a result, gas separation by membrane process has attained high importance in the industrial setting in terms of cost-effective considerations, as gases occupy a fundamental point in the chemical feed stock industry. Current applications of membrane-based gas separation include oxygen and nitrogen enhancement, hydrogen purification and recovery, natural gas separation, removal of carbon dioxide from flue gas and volatile organic compounds from effluent streams [3] [7] [8]. For porous membranes, the International Union of Pure and Applied Chemistry (IUPAC) approvals [9] [10] membrane pores are categorized into three distinct types: micropores having diameter less than 2 nm, mesopores, diameter greater than 2 nm but less than 50 nm and macropores with diameter more than 50 nm [11]. Practically speaking, investigational gas adsorption isotherms usually fall into six groups. Most importantly, adsorption isotherms for microporous solids tallies with types I while types IV and V isotherms corresponds to features of mesoporous solid materials which are characteristic of mesoporous solids (especially ceramics). Additionally for the type VI and V, the adsorption process indicates macroporous solids, but at an elevated relative pressure, the amount of adsorption increases sharply due to the capillary condensation mechanism in the mesopores [12] [11]. The objective of this paper is to discuss the Structural characteristic and permeation of gases through a supported silica inorganic ceramic membrane. It is a well-known fact that ceramic membranes are better supports due to their superior thermal and mechanical properties. This allows for operation at higher temperatures and transmembrane pressure differences.

II. EXPERIMENTAL

A. Structural characteristics of membrane pore network

The structural characterisation of support and modified membranes was done by employing probe molecules in this case nitrogen at a low temperature of 77k to adsorb the pore walls within the membrane pores. These measurements were acquired using Gas sorption system analyser (Quantachrome

Instruments Florida, USA). The isotherms are plotted in fig. 4 and fig. 5. However, before this was done, the process of degassing was carried out to remove unwanted material present by subjecting the surface of the membrane material to an elevated temperature of about 300°C. A difference in the weight before and after degassing was also obtained. Due to its simplicity the Brunauer-Emmett-Teller (BET) gas adsorption model which has become the most widely exploited technique used for the determination of the surface area of finely-crushed sample of support and modified membrane. To enable accurate evaluation, gas adsorption isotherms and hysteresis are displayed in graphical form with the amount of nitrogen adsorbed plotted against the relative pressure as shown in fig. 1 and 2 [13].

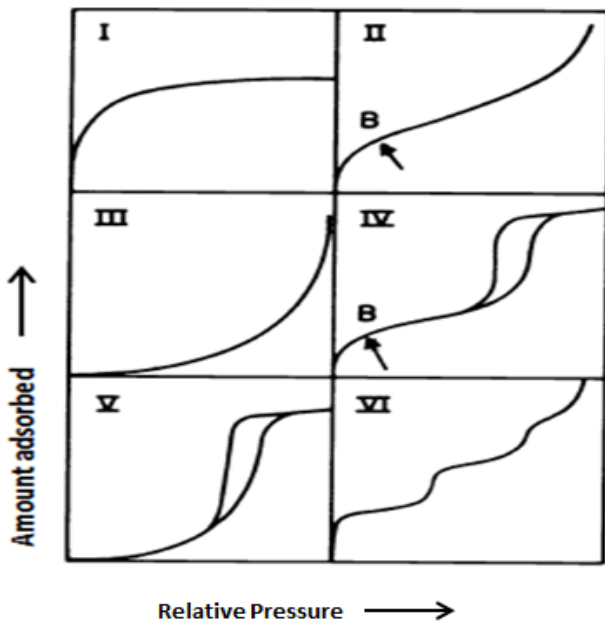


Fig 1: The various kinds of physisorption Isotherms

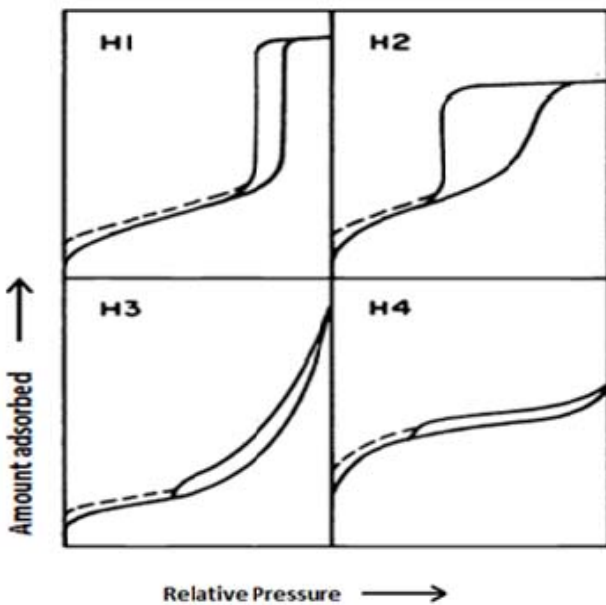


Fig 2: Types of Hysteresis

III. GAS PERMEATION TEST

The gas permeation experiment was performed using the supported silica inorganic membrane prepared using a successive dip-coating procedure [14] to achieve the desired membrane pore size modification. This process is a patented innovation from a well-known inventor and researcher [15] [16]. The commercial alumina support layer has an i.d. = 7 mm, o.d. = 10 mm and nominal pore diameter of 15nm with an impermeable 5cmat both ends. Single gas permeation through the membranes was measured at 298 and 373K and the gases used for the gas transport tests include: nitrogen (N₂), hydrogen (H₂), argon (Ar) and methane (CH₄) respectively. The gases were delivered by BOC, UK. A Pictorial view of the supported silica ceramic membrane is shown in fig. 3. For the purpose of this work, the gas permeance F was determined using the expression shown in equation 1.



Fig 3: Pictorial view of the silica ceramic membrane.

$$F = \frac{Q}{A\Delta P} \quad (1)$$

Where Q is the gas flux (mol/sec), A is the membrane surface area (m²) and ΔP is the pressure difference (pa)

IV. RESULT AND DISCUSSION

The structural characteristic of the support and the supported silica membrane were analyzed using nitrogen adsorption method to determine the surface and the pore size distribution. The plots of the amount of gas adsorbed (volume at STP (cc/g) against relative pressure (P/P₀) is shown in in fig. 4 for support and fig. 5 for the silica supported membrane. As observed, two colors are shown in the plots. The blue which depicts desorption line and the red which represents the adsorption trend line. The hysteresis of the fresh membrane in fig. 4 has a close resemblance to type H1 loop in figure 2 above. The adsorption and desorption lines are identical, thus according to [13] indicates that the membrane has large pores which are features of support. For the silica supported membrane in fig. 5, it can be seen that there is an enlargement in the loop similar to that of type IV isotherm where the adsorption process initiates, but at an elevated relative pressure, the amount of adsorption increases sharply due to the capillary condensation formation in the mesopores, this is in accordance as reported by [13]. This result is similar to work done by [17]. Another group of researcher [18] in their work utilized modified silica membrane which demonstrated a type IV isotherm established on the BET arrangement, indicative of isotherm typical of adsorption on mesoporous solid which is

considered by the hysteresis as presented. The BET summary and BJH method of desorption for support and silica membrane are shown in table 1. From multi points chosen at random, plots obtained gave a surface area of 0.161m³/g for the support and 1.068m³/g for the silica membrane. This change in the membrane surface area suggests that the silica modification has had an effect on the support. Further investigation on the determination of the pore diameter of both the support and silica membrane was carried out. The result further confirms the pore diameter determined using the Barrette-Joyner-Halenda (BJH) method of desorption. From the values obtained, there was a clear difference between the pore diameter of support (4.182nm) and the pore diameter after modification (3.136nm) indicating the characteristic features of a mesoporous membrane of pore diameter. (Between 2nm and 50nm).

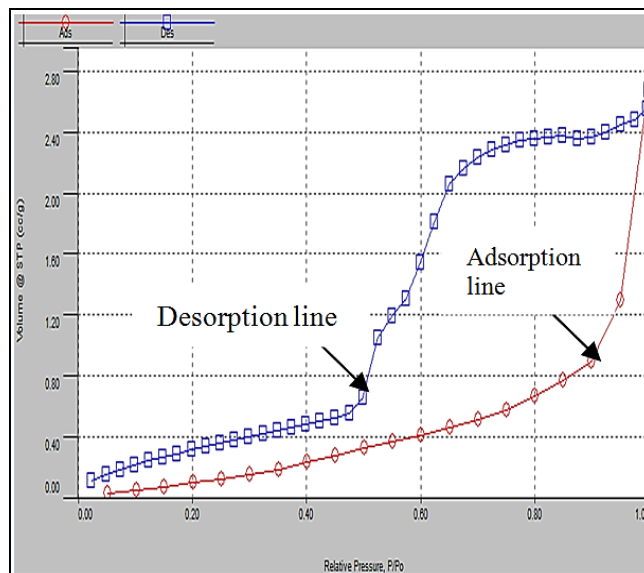


Fig 5: Plot of Linear Isotherm of Gas Adsorption and Desorption for silica membrane

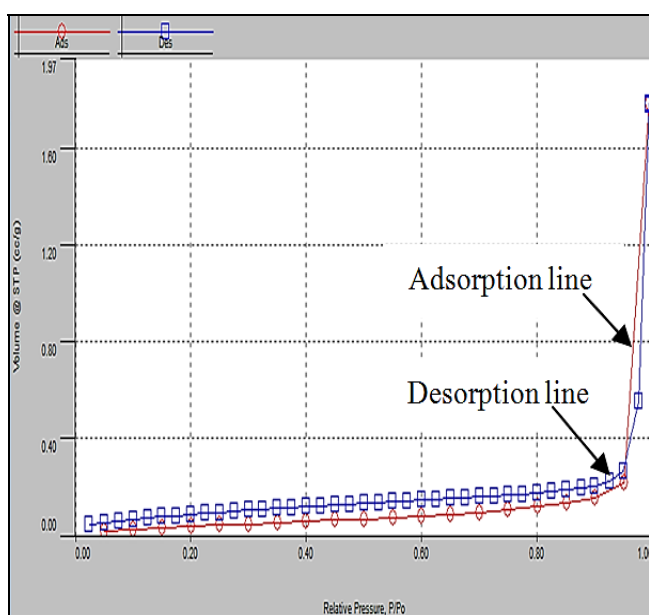


Fig 4: Plot of Linear Isotherm of Gas Adsorption and Desorption for fresh membrane

TABLE I			
BET SUMMARY AND BJH METHOD OF DESORPTION FOR SUPPORT AND SILICA MEMBRANE			
	Support	Silica Membrane	
Surface Area	0.161	1.068	
Pore Diameter	4.182	3.136	

The differences in single gas permeances versus the mean pressure given as $P_1 + P_2/2$ through the supported silica membrane were studied. Fig. 6 and fig. 7 shows the relationship between H₂, N₂, CH₄ and Ar permeances and the mean pressure at a temperature of 298K and 473K within the pressure range tested. As can be observed H₂ gas maintained the highest permeance with rise in temperature. Again individual gas permeance decreased with the mean pressure, in this scenario; viscous contribution is not quite relevant. However all indication tends towards Knudsen diffusion mechanism which occurs when the mean free path of the gas molecules is much bigger than the pore diameter of the membrane pore walls through which the gases permeate. In this circumstance, the gases with lower molecular weight will be favoured which can be identified in mesoporous.

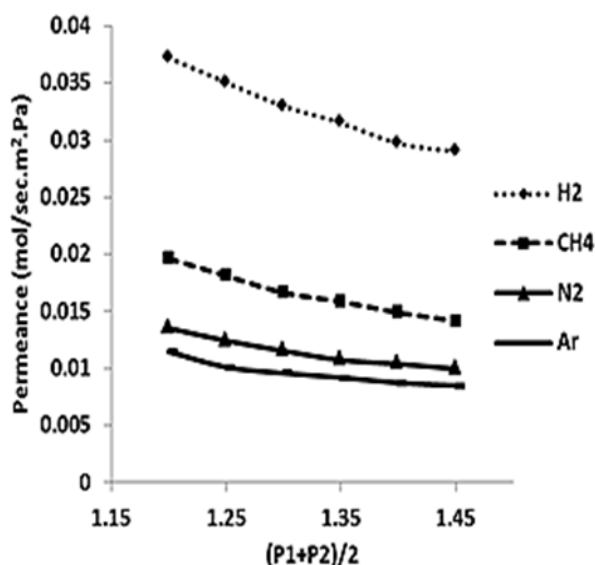


Fig 6: H₂, CH₄, N₂ and Ar permeance as a function of mean pressure at 298K

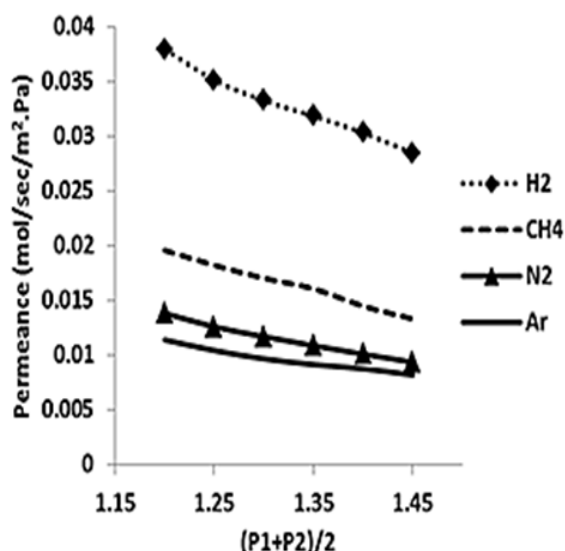


Fig 7: H₂, CH₄, N₂ and Ar permeance as a function of mean pressure at 473K

V. CONCLUSION

The structural characterization and pore distribution of a commercially available support coated with silica based solution using BET and BJH models have been studied. The BET summary is from multi points chosen at random gave a surface area of 0.16m³/g for the support, whereas, for the supported silica membrane, there was an increment in the surface area to 1.068m³/g. The silica membrane exhibited a type IV/V isotherm indicating that the membrane has a mesoporous membrane characteristic at a temperature of 77 K. This also shows that there is a significant influence of the silica modification of the support. From the values

obtained, with respect to the pore size distribution, there was a clear difference between the pore diameter of the support (4.182nm) and the pore diameter after modification (3.136nm) indicating the characteristic features of a mesoporous membrane of pore diameter between 2nm and 50nm in agreement with literature. Permeation experiments conducted at temperatures 298K and 473K, in relation to the mean pressure show that the supported silica membrane can operate at high temperatures. Results of this study demonstrate the potential for using this membrane in membrane reactors including applications that require operation at relatively high temperatures.

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