Hydrogen permeation using nanostructured silica membranes

M. N. Kajama, N. C. Nwogu & E. Gobina
Centre for Process Integration and Membrane Technology (CPIMT),
School of Engineering, Robert Gordon University, UK

Abstract

This study examines hydrogen (H_2) transport and separation factors for various gases on mesoporous membrane for unmodified and dip-coated silica membrane. Single gas permeation of H_2, N_2, CH_4, Ar and CO_2 were determined at permeation temperature of 298–373 K and feed gauge pressure of 0.1 to 0.9 barg. H_2 permaetion rose from 3.3 to about 6.4 l/min at 0.9 bar. H_2 selectivity over N_2, CH_4, Ar and CO_2 for the dip-coated silica membrane at 298 K and 0.9 bar was 2.93, 2.18, 3.51 and 3.61 respectively. Observation of the permeation of these membranes revealed that the transport of gases is governed by a combination of activated transport and knudsen flow.
Keywords: mesoporous membranes, dip-coating, gas permeation, hydrogen selectivity, permeation temperature.

1 Introduction

Nearly 80% of the energy demand worldwide comes from fossil fuels, i.e. oil, natural gas and coal. Unlike using fossil fuels, hydrogen produces only water as byproduct [1]. The global energy consumption is forecasted to rise by 56% from 2010 to 2040 [2]. This has prompted research to alternative such as hydrogen as a substitute for the current fossil fuels because it is widely accepted as a clean energy carrier for instance in the utilization of fuel cell systems and these could help to address the problems linked to energy security which includes air pollution and global climate change. The state-of-the-art inorganic membranes have emerged as an attractive substitute in gas separation application, particularly for hydrogen separation from process streams due to their thermal, chemical and mechanical stability when compared with polymer membranes. In the last five decades,

modern membrane science and technology was advanced and sufficient knowledge regarding their structures and function in gas-separation was documented [3].

A membrane is basically a barrier that is selective to specific component and hinders others to pass through (Fig. 1) and is driven by a concentration difference across the membrane. Membranes are widely used for purification in industries e.g. waste water treatment, pharmaceuticals, food, and biochemistry [4]. Membrane technology has gained acceptance for gas separations such as carbon dioxide separation from fuel gas [5], hydrogen separation recovery for fuel cell application [6], ethylene recovery in ethylene oxide, gasoline vapour recovery [7] and recovery of methane from bio-gas [8].
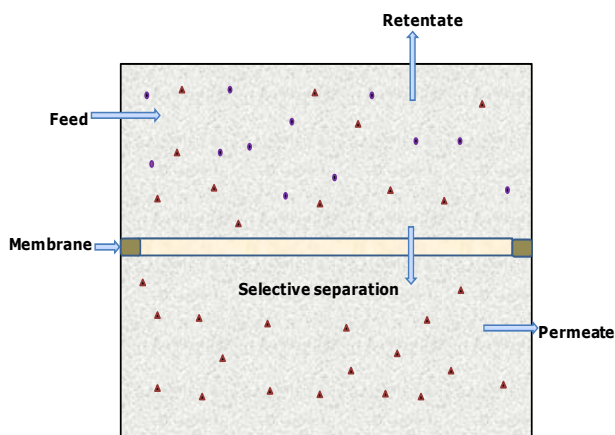

Figure 1: Membrane design.

Membrane gas separation has a lot of advantages features when compared to other gas separation processes such as adsorption, absorption, cryogenic distillation. The features include compact and light weight, easy to operate and maintain, no phase change, environmentally benign, cost-effective and energy efficient [9].

According to IUPAC, inorganic membranes are classified as; Micropores 0.5–2 nm where separation is based on molecular sieving mechanism, mesopores 2–50 nm where Knudsen flow mechanism is the dominant flow but multilayer flow and/or capillary condensation and viscous flow can also take place, and macropores > 50 nm where there is no separation and the flow mechanism is basically influenced by viscous flow [10–12]. In fact, permeability and selectivity are the main basic properties of a membrane.

Permeability is termed as the flux of a specific gas component through the membrane per unit of area at a given pressure gradient taking into account the membrane thickness [13, 14] and is usually written as shown in equation (1).

$$P_e = qL/A\Delta P \qquad (1)$$

where P_e is the Permeability (mol-m/m^{-2} s^{-1} Pa^{-1}), q is the molar flow (mol/sec), A is the surface area of the membrane (m^2), ΔP is the pressure difference (Pa) across the membrane and L the thickness of the membrane (m).

Selectivity is the ability of the membrane to separate (select) the required component from the feed mixture [14]. Pure gas selectivity is defined as the ratio of the single gas permeabilities (P_y and P_z). It can be written as;

$$\alpha_{y,z} = P_y/P_z \tag{2}$$

where P_y is the permeability of y component (mol-m/m^{-2} s^{-1} Pa^{-1}), and P_z is the permeability of z component (mol-m/m^{-2} s^{-1} Pa^{-1}).

Porous ceramic membrane's characterization is typically elaborated by the flux and the selectivity which are influenced by the pore size distribution, intrinsic membrane surface properties and porosity [15]. Nitrogen adsorption-desorption isotherm (77 K) is a standard technique employed to characterize the pore structure and network of a material. It is perhaps simple and the most widely used method to determine the specific surface area, pore size and pore size distribution for meso and microporous adsorbents [15, 16]. The gas adsorption isotherm is divided into six categories [15–17] as shown in Fig. 2. Five of the six categories are mentioned in the IUPAC recommendations [16]. Types IV and V are the most significant isotherms which are typical characteristic of mesoporous solids proceed through monolayer and multilayer hysteresis followed by capillary condensation [15, 16] during desorption, and type I is categorized under microporous solids [15].
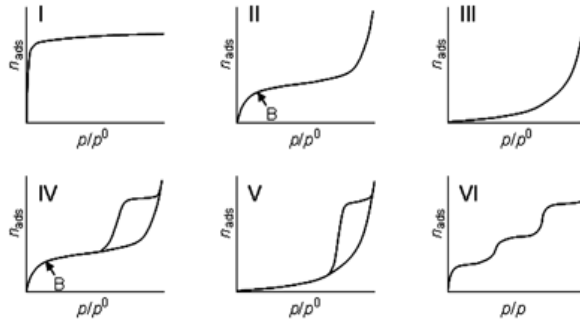

Figure 2:   Different types of physisorption isotherms as observed for different adsorbents. Type I: microporous; Type II: non-porous or macroporous; Type III: non-porous or macroporous with weak interaction; Type IV: mesoporous; Type V: mesoporous with weak interaction; Type VI: layer-by-layer adsorption. The point B refers to monolayer adsorption capacity from which the surface area of the sample can be determined [15, 17]. *Note: P/P^0* = Relative pressure, n^{ads} = Amount adsorbed.

Inorganic membranes for H_2 separation are commonly made from metal oxide or sintered metal, palladium metal, zeolite and silica [18]. Silica membranes are candidates for H_2 separation which have been prepared using either sol-gel or

chemical vapour deposition (CVD) methods. Literature shows that silica membranes provides a permeance between (10^{-7}–10^{-9} mol.m^{-2}s^{-1}Pa^{-1}) for hydrogen and also presented satisfactory selectivity (100–3000) above N_2 [19, 20]. Kim et al. [21] prepared microporous (with pore size < 2 nm) silica membranes from a 150 nm porous α-alumina tube and obtained a hydrogen permeance of 2×10^{-7} to 7×10^{-7} mol.m^{-2} s^{-1}Pa^{-1} at permeation temperature of 573 K, and a separation of about 11 and 36 for H_2/CO_2. Similarly, Asaeda and Yamasaki [22] fabricated a porous silica membrane coated on top of cylindrical porous α-alumina tube prepared by hot coating also obtained a hydrogen permeance of 1.3×10^{-6} mol.m^{-2}s^{-1}Pa^{-1} and a H_2 selectivities of 150, 1100 and 6300 over CH_4, C_2H_6 and C_3H_8 at the same permeation temperature. Lee and Oyama [19] also prepared a nanosil silica membrane from a 4 nm vycor support showing higher hydrogen permeance with a selectivity of 10^4 over CO_2, CO and CH_4 at a permeation temperature of 873 K. It is however reported by Gu et al. [23] that a hydrogen permeance of 2 to 3×10^{-7} mol.m^{-2}s^{-1}Pa^{-1} was obtained on the same temperature with selectivity factors 590, 700, and 940 for H_2/CO_2, H_2/CO and H_2/CH_4 respectively. Recently, Amanipour et al. [24, 25] prepared a hydrogen-selective nano-composite ceramic membrane by CVD method and obtained a H_2 permeance of 6.30×10^{-7} mol.m^{-2}s^{-1}Pa^{-1} following a deposition for 6 hours and a H_2 selectivity over N_2 from 5.6 to 203. Also, selectivity of 105 and 573 were obtained for H_2/CO_2 and H_2/CH_4 at a permeation temperature of 1073 K.

The aim of this work therefore is to use a silica membrane for hydrogen separation from natural gas at different temperatures and pressures. The effects of permeation properties including gas molecular weight and gas kinetic diameter are examined.

2   Experimental

2.1   Membrane preparation and characterization

Commercial mesoporous alumina supports of tubular configuration supplied by CTI (France) consisted of 77% alumina and 23% TiO_2 was employed for this experiment. The alumina support had an internal and outer 7 and 10 mm diameter respectively. It possesses a permeable length of 348 mm and 45% porosity. Pressures of 0.05 to 0.9 bar and temperatures of 298 K to 573 K were applied.

The membrane was prepared using the dip-coating method on the 15 nm support by mixing 50 ml of silicon elastomer (Sylgard®) and nine parts of isopentane contained in a glass tube to obtain a clear and colourless solution. A curing agent (Sylgard®) equivalent to one-tenth of the elastomer was added and the resulting solution was mixed at room temperature. The solution was then allowed to age for 30 minutes after which the ceramic support was immersed for 30 minutes. The membrane was then oven dried at 65°C for 24 hours [26, 27] to form an ultra-thin layer on the support. The same procedure was repeated for subsequent coatings. Up to five dip-coated membranes were prepared and evaluated in this experiment.

2.2 Experimental set-up and procedure

The experimental set-up consisted of a membrane reactor, gas delivery system for pure gases and gas mixtures, a permeate and retentate exit, a flow meter and thermocouples fixed on the reactor as shown in Fig. 3. However, all connections were tested for leaks by means of a soap solution. The gas species used in the experiments consisted of single gases CH_4, CO_2, H_2, He, N_2 and Ar (BOC UK) with at least 99.999 (% v/v) purity.
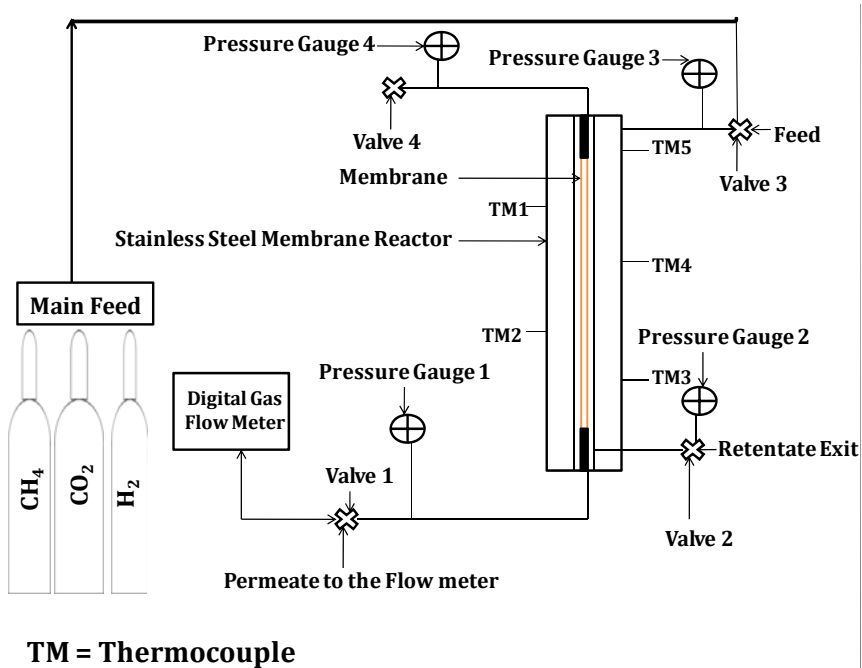

Figure 3: Schematic diagram for the experimental rig.

In a typical experiment, the gas was passed into the shell-side and permeated through the coated membrane at different pressures. The permeate was connected to the flowmeter to measure the flow rates.

2.3 Characterization of the membrane

The Brunauer-Emmett-Teller (BET) method for surface area, Barrett-Joyner-Helanda (BJH) method for pore size distribution, and the nitrogen adsorption-desorption isotherm of unmodified support and silica modified membrane were obtained from N_2 sorption isotherm (1994-2012 Quantachrome instrument version 3.0). Prior to N_2 sorption analysis, crushed weighted samples were degassed for 180 min at 300°C at a rate of 10°C/min.

3   Results and discussion

3.1 Structural characterization of the membrane

The N_2 adsorption-desorption isotherms of silica modified membranes are shown in Figs. 4 and 5. The adsorption-desorption isotherms exhibits a characteristics of mesopores solids (especially ceramics) resulting with type IV and V physisorption isotherm undergoing capillary condensation and hysteresis during desorption [15]. Different parameters were obtained for the Brunauer-Emmett-Teller (BET) method surface area and Barrett-Joyner-Helanda (BJH) method pore size distribution on this study. The BET surface area and BJH pore diameter were 0.364 m^2/g and 4.171 nm for the unmodified support (not shown) and 0.439 m^2/g and 4.179 nm for the silica membrane respectively. BET surface area increased to about 0.484 m^2/g after subsequent dipping. BJH pore diameter also decreased from 4.171 to 3.940 nm which indicates that some amount of silica has been deposited into the membrane and resulted with pore size reduction.
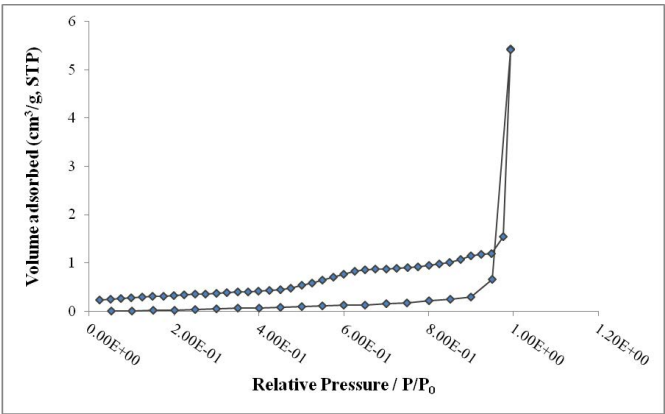

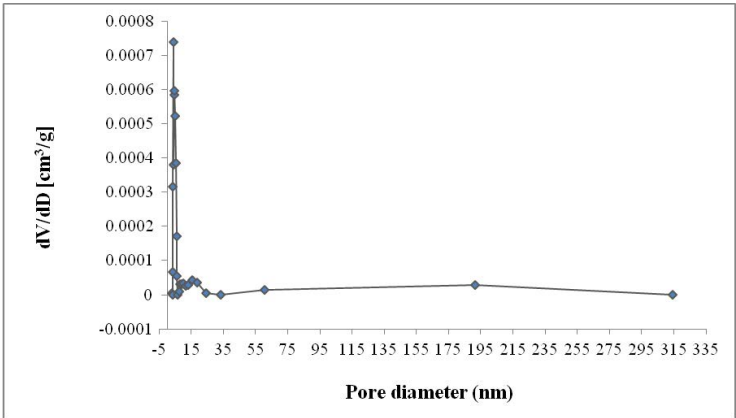Figure 4: N_2 adsorption-desorption isotherm for silica membrane.

Figure 5: Pore size distribution for silica membrane.

3.2 Gas permeation

Fig. 6 shows the single gas permeation results of the dip-coated silica membrane. The permeation of molecules with smaller molecular weight such as H_2 was higher than those of the larger molecules like N_2 and CO_2. These results are indicative of molecular weight dependent transport mechanism of H_2 separation from natural gas.
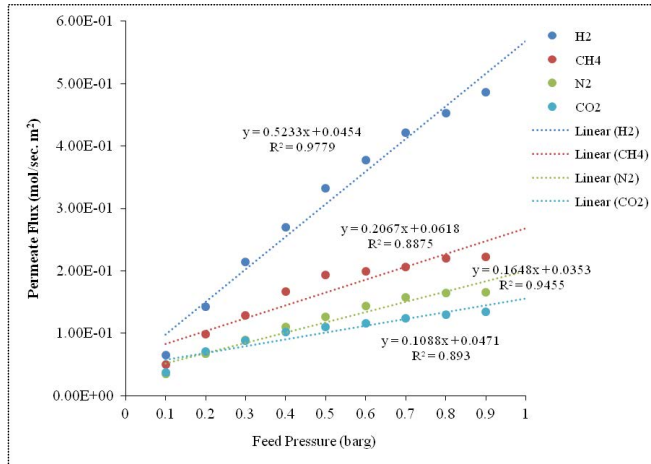

Figure 6:   Gas permeate flux graph for modified membrane vs feed pressure at 298 K.

Fig. 7 shows the permeation relationship of H_2 molecule to feed pressure for unmodified and dip-coated silica modified membranes at 298 K. It can be seen that after silica deposition, H_2 permaetion rose from 3.3 to about 6.4 l/min at 0.9
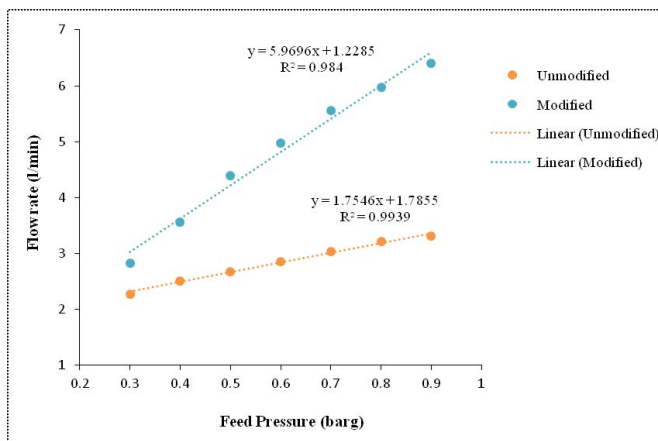

Figure 7: H_2 permeation for unmodified and modified membranes vs feed pressure at 298 K.

bar. H_2 selectivity and viscosity ratio over N_2, CH_4, Ar and CO_2 for the dip-coated silica membrane at 298 K and 0.9 bar was obtained as 2.93, 2.18, 3.51 and 3.61 and 0.50, 0.80, 0.39 and 0.60 (Table 1). This shows a clear indicative that H_2 selectivity over these gases are close to that of ideal knudsen when compared to viscous flow mechanism.

Table 1: H_2 selectivity at room temperature and 0.9 bar.

Hydrogen selectivity at 298 K and 0.9 bar			
Gas	H_2 selectivity	Viscosity (μ Pa s) ratio	Ideal Knudsen selectivity
H_2/N_2	2.93	0.50	3.74
H_2/CH_4	2.18	0.80	2.83
H_2/Ar	3.51	0.39	4.47
H_2/CO_2	3.61	0.60	4.69

Helium and nitrogen permeation decreases with increasing temperature at 0.4 bar (Fig. 8). These results are indicative of Knudsen flow transport mechanism.
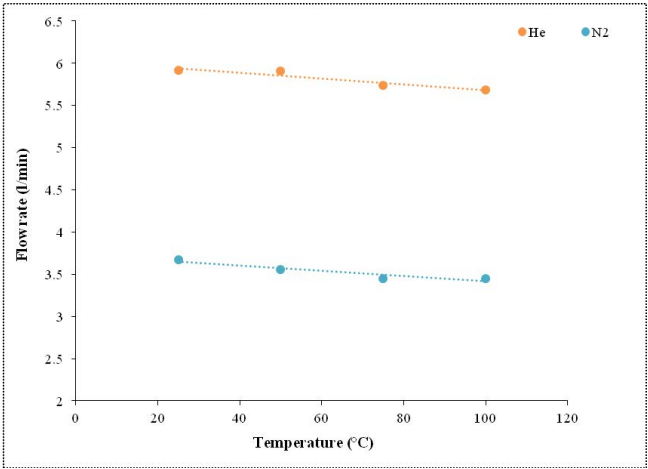

Figure 8: He and N_2 permeation for modified membrane vs permeation temperature at 0.4 bar.

4 Conclusions

The studies have shown that the permeation behaviour of gas molecules H_2, N_2, CH_4, Ar and CO_2 on dip-coated silica membranes can be described on the basis of Knudsen flow transport mechanisms.

Acknowledgement

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