Hydrogen Separation using Silica Membranes
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Abstract: - Silica membranes were synthesized on tubular supports of alumina by dipping in silica colloidal solutions. The quality and the performance of the silica membranes were tested by experiments on single gas permeation and gas separation of mixed N \textsubscript{2}, CO \textsubscript{2}, CH \textsubscript{4} and H \textsubscript{2}. The membranes were able to separate H \textsubscript{2} selectively from a binary mixture gas. Scanning Electron Microscope and Gas Permeation were used to characterize the silica membranes.

Key-Words: - Hydrogen separation, Silica membranes, Colloidal solution, Gas permeation, Knudsen diffusion

1 Introduction
Nowadays, about 80% of the present world energy demand comes from fossil fuels. However, on the one hand, fossil fuels produce pollution compounds such as carbon monoxide and carbon dioxide among others. On the other, hydrogen is well known as the clean fuel of the future [1, 2]. There are several processes to produce hydrogen, but the most important industrial process is catalytic steam reforming of hydrocarbons on nickel catalysts [3, 4]. Although this process is a mature technology, it is somewhat complex as it contains many steps and it additionally produces CO, H \textsubscript{2}O and CO \textsubscript{2}. Still, the main disadvantage is that the obtained H \textsubscript{2} is not pure enough to be used in advanced applications such as PEM fuel cells where H \textsubscript{2} must be free of CO. Pt electrodes have to be free of poisons.

Three main processes for hydrogen separation are known, namely PSA, cryogenic distillation, and membrane separation. The PSA process, by far, is the most extensively used in industrial processes. The PSA units are based on the adsorbent capacity to retain more impurities at high gas partial pressure than at low gas partial pressure. These systems are commonly used in the chemical and petrochemical industries. Extensive studies have been done in this area since the 1970s [5]. Membrane processes are considered to be one of the most promising technologies for the production of high-purity hydrogen [6]. They can provide an attractive alternative to PSA and cryogenic distillation, depending upon the purity and scale of production. Furthermore, membrane separation processes consume less energy with the possibility of continuous operation [7]. A membrane is a thin, permeable interface used to separate two regions in a chemical system. In industrial chemical processes, a membrane can be used to separate compounds depending on the size of the molecule, the differences of molecules solubility in the membrane, the dissociative diffusion mechanisms, or other processes. For hydrogen production and purification, there are generally two classes of membranes both being inorganic: dense phase metal, metal alloys and ceramics (perovskites), and porous ceramic membranes. Porous ceramic membranes are usually prepared by sol–gel or hydrothermal methods, and they have high stability and durability at high temperature. So the field of inorganic membrane science is an attractive area for research, with emphasis on the relevance of porous inorganic membranes for chemical process industry [8, 9]. Many important applications of inorganic membranes are related to energy or environment in industrial processes. Much effort has recently been devoted to the synthesis of inorganic membranes because of their potential applications in the domains of gas separation, pervaporation, and reverse osmosis, as well as in the development of chemical sensors and catalytic membranes [10-14]. Inorganic membranes, which possess good thermal stability and chemical inertness, present several important advantages over polymeric membranes for many industrial applications. Improvements continue to focus on areas of membrane integrity and manufacturing costs. Among developed inorganic membranes, amorphous silica membranes are most attractive for gas separation at elevated temperatures since they are stable under crucial conditions where polymeric membranes cannot be applied. The chemical and thermal stability
of silica membranes are advantageous if compared to those of organic membranes. These features determine that silica membranes turn out to be interesting candidates for separation of permanent gases in chemically and thermally aggressive environments [15-16]. Several methods to synthesize silica membranes have been reported in the last two decades. For example, Gavalis et al [17] first succeeded to cover a Vycor glass tube with a silica whose pore size was of about 4 nm, the silica was produced by chemical vapour deposition (CVD) [18,19]. Others methods to prepare microporous silica membranes is sol-gel and dip-coating [20, 21]. Improvements in the synthesis of supported silica membranes have resulted in very thin defect free layers [22, 23].

In this work, silica membranes supported on alumina tubes were prepared by dipping in silica colloidal solution. The silica membranes were characterized by scanning electron microscopy to determine morphology and textural properties. The separation capacity was tested by single gas permeation with H2, CO2, N2 and CH4. The H2 selective separation from gas mixtures was also measured.

2 Experimental
Silica membranes were prepared on porous tubes (7 mm i.d. and 10 mm o.d. and 250 mm of length) of alumina (Membralox® Pall Corp. 0.2 microns average porous size). The precursor solution was colloidal silica (Ludox, AS-40) containing uniform spherical particles with a size of 14 nm approximately and having a specific surface area of 220 m²/g. First, colloidal silica was diluted with distilled water to obtain a 15 %w silica solution then the colloidal silica was peptized using a polyvinyl alcohol solution (12 %w) mixing under vigorous stirring for 2 h. The membranes were obtained by dipping the tubular support into the silica solution for 1 h and then dried at 100°C into an oven for 1 h. The above procedure was carried out 5 times until both, weight gain and N2 permeation, were maintained without change. The adherence between the formed silica layer and the alumina support was obtained by calcination at 800°C for 6 h. For the permeation experiments, the silica membranes were placed inside a quartz separation module and sealed with Teflon o-rings, the permeation zone in the membrane was approximately 200 mm long because both ends of the tube are smelted 25 mm each. Two types of permeance measurements were performed, i.e., single gas dead-end permeance, using H2, N2, CO2 and CH4 and gas separation measurements in the binary gas mixtures above mentioned. A mass-flow controller (Brooks) was used to measure gaseous feed stream containing 100 mL/min of an equimolar mixture H2/N2. The gas mixture was fed to the tube side (retentate) of the membrane, while the shell (permeate) side stream was sent to the GC Analysis. The pressure difference between both sides of the membrane was monitored by means of two pressure gauges, and the composition of the retentate and permeate streams was analyzed by online gas chromatograph (TCD, Varian 3700). In addition, the membranes were characterized by SEM (Leica Stereoscan 440) to observe the morphology of layer silica on the alumina support.

3 Results and discussion
Since permeance is normally enhanced through the sacrifice of selectivity, a balance between permeance and selectivity is essential to achieve optimum performance. Figure 1 shows the amount of silica deposited on the tubular support, the total amount of silica deposited was 125 mg (full squares) approximately along the full tube length, after five dipping cycles. Note that after three dipping cycles the weight gain was not significant (full circles).

![Fig. 1 Amount of silica deposited on the tubular support](image)

Figure 2 shows SEM images of (a) the alumina porous support before the deposition of the silica particles, (b) the cross section of the silica membrane (film), after five dipping cycles where two regions can be observed, one corresponding to the grains of the alumina support and the other to the silica layer on the support. The silica layer deposited on the alumina tube was homogeneous and smooth.
without surface defects as pinholes or cracks, the thickness of the silica layer was 1µm. The silica membrane was firstly tested by single gases such as H₂, CO₂, CH₄ whose dead-end permeance was measured at room temperature. In a dead-end permeance measurement, a pressure difference over the membrane is applied and the stationary flow necessary to maintain the pressure difference is determined. Figure 3 shows the experimental results of the single gas permeation through the membrane versus the pressure drop. In this figure, it is clear that the H₂ permeation is higher than for other gases. The silica membrane was tested in gas separation experiments with a mixture of H₂/CH₄ at room temperature as a function of the CH₄ partial pressure. The results are presented in Figure 4. In this figure, the permeance of H₂ is higher than CH₄ permeance, besides the behavior of H₂ permeation is homogeneous and stable; thus, CH₄ partial pressure increased. Instead, CH₄ permeation is very heterogeneous due to adsorption effects between CH₄ and the membrane. Lastly, an experiment at high temperature was carried out, where the permeance...
values of the mixture of $H_2/N_2$, are studied as a function of pressure drop. In the system $H_2/N_2$ it was carried out at 400ºC and the results are presented in Figure 5. Here, the $H_2$ permeance values are in the range 5 to $9 \times 10^{-7}$ mol-m$^{-2}$-Pa$^{-1}$-s$^{-1}$ and they were higher than $N_2$ permeance values. Furthermore, they depend almost linearly on the pressure drop. In contrast, $N_2$ permeation ($1.1 \times 10^{-7}$ mol-m$^{-2}$-Pa$^{-1}$-s$^{-1}$) was almost constant in all the range of pressure drop studied. As it is well known [24, 25], the gas permeation of permanent gases like $N_2$ and $H_2$ through porous inorganic membranes follows a typical Knudsen diffusion and the theoretical relative separation factor is 3.74 for the gas mixture $H_2/N_2$. Therefore, using the permeance results presented in Figure 4, the calculated relative separation factor is ~ 5, which is higher than the theoretical value.

4 Conclusion
Silica membranes were prepared on an alumina tubular support using silica particles dispersed as a colloidal solution. After calcination, a homogeneous and smooth layer of silica was deposited. It was verified by single gas permeation that the membrane could be suitable for gas separation. Finally, $H_2$ was selectively separated both as single permeation and from a mixture of $H_2/N_2$ $H_2/CO_2$ $H_2/CH_4$. One experiment using a mixture of $H_2/N_2$ was carried out at high temperature; the membrane presented a $H_2$ permeation, five times higher for $H_2$ than for $N_2$. Thus, this silica membrane is able to separate $H_2$ at room temperature and at high temperature. Then, this membrane can be use as extractor reactor during the $H_2$ production using membrane reactor.

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References:


