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# NaA zeolite membranes synthesized on top of APTES-modified porous stainless steel substrates

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NaA zeolite membranes were synthesized on top of both disk and tubular porous stainless steel substrates by the secondary growth method. The support seed stage was optimized, considering the seed synthesis conditions and the deposition method. The formation of the NaA zeolite on both the membrane and the residual powder collected at the bottom of the vessel after synthesis was corroborated by X-ray diffraction (XRD). Scanning electron microscopy (SEM) revealed the formation of a film with well-defined crystals with a cubic morphology characteristic of the NaA zeolite. The support modification with 3-aminopropyltriethoxysilane improved the morphology and stability of the NaA zeolite membranes synthesized on top of porous stainless steel substrates. When vacuum was applied only in the last hydrothermal synthesis stage, a smooth zeolite layer was obtained on top of porous stainless steel supports. The single gas ($H_2$, $N_2$, $CO_2$ and $CH_4$) and mixture ($H_2/N_2$ and $H_2/CH_4$) perm-selective properties of the tubular membranes were evaluated as a function of temperature and pressure. Separation factors higher than the Knudsen coefficient were obtained in all membranes. The single gas $H_2$ and $CO_2$ permeation flux of the membranes increased with temperature indicating a preponderance of the activated diffusion over the Knudsen diffusion. The higher $H_2/CO_2$ ideal separation factors were 7.6 and 5.6 for the more selective tubular membranes, at 453 K and 100 kPa.

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## 1. Introduction

Spurred by the increasing interest in the development of alternative processes for hydrogen production and its use as an energy carrier, the potential of membrane-based technologies is considered to be most promising. High efficiency, cost reduction and greater flexibility of operation can be achieved using a hydrogen-selective membrane to extract hydrogen from the membrane reactor that combines the reaction and separation in the same vessel [1]. Besides being used as an energy carrier, hydrogen is employed as feedstock in several industrial processes from chemical and metallurgical to petrochemical, electronics and glass.

Membranes for hydrogen purification can be classified as metallic (pure metals or alloys), polymeric and porous inorganic. Within them, palladium-based membranes exhibit high hydrogen permeation and almost infinite selectivity [2]. However, they present serious drawbacks if applied at low temperatures ($<573$ K). Compared with commercially available dense palladium-based membranes, zeolite membranes exhibit a higher hydrogen permeation flux and a moderate selectivity. Due to properties such as uniform pore structure, high adsorption capacity, catalytic activity, thermal stability and chemical resistance, zeolite membranes are promising materials to be applied for hydrogen purification from several processes [3, 4]. Different types of zeolites including MFI [5,6], DDR [7], LTA [8] and FAU [9] have been reported as membranes for liquid or gas purification. The selection of a suitable zeolite structure for a particular application depends on the affinity of the zeolite towards the specified molecules to be separated. Among these membranes, the LTA zeolite is especially attractive considering its hydrophilic framework and pore size (0.4 nm). The LTA zeolite membranes are mostly used in the dehydration of water-organic solutions by pervaporation or vapor permeation [10]. Furthermore, these membranes have potential for the separation of a small molecule as hydrogen; nevertheless, there are few publications reporting successful shape-selective separation using LTA membranes.

According to the gel composition, the NaA zeolite hydrothermal synthesis can be classified [11] into: (i) concentrated gel, (ii) clear solution without template and (iii) clear solution with a structuring agent. Using a concentrated gel throughout the different synthesis, a continuous well-intergrown NaA zeolite layer was obtained on top of ceramic tubes. On the other hand, when a clear solution was used in the last hydrothermal synthesis stage, a layer of weakly intergrown zeolite crystals was observed [11].

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The synthesis of supported defect-free zeolite membranes is still a challenge even though different methods have been developed to improve the quality of the films. The most promising preparation method for zeolite membranes is the secondary growth method [12,13], mainly aimed to cover the surface of the support with a layer of zeolite seeds. Subsequently, a hydrothermal treatment is carried out on the seeded support to favor crystal growth. Therefore, by decoupling zeolite nucleation from crystal growth, the optimization of the conditions of each step is independently allowed. This methodology enhances the crystallization kinetics, avoiding the nucleation step and has important implications such as shorter synthesis times for a continuous zeolite layer to grow on the support, more easily achieved preferential orientation, and thinner zeolite layers [14]. Thus, this method has potential advantages in terms of reproducibility and control of membrane structure if compared with the in situ synthesis method [15]. The amount of nuclei and their uniform distribution on the surface should be optimum considering that they act as nuclei for zeolite film growth; consequently, the seed size, orientation and coverage are significant for the control of the membrane morphology. To improve the membrane performance, the use of covalent linkers as APTES and 1,4-diisocyanate between the zeolite layer and the alumina support has been report [9,10]. These molecular linkers promote the attachment and anchoring of the precursor to the support improving the nucleation and growth of the zeolite layer.

As it is well known, the properties of synthesized membranes significantly depend on the physical structure and chemical characteristics of the support. Taking into account factors such as cost, thermal conductivity, anticorrosion quality and mechanical strength, stainless steel is a very promising support for a composite membrane. For the synthesis and applicability of composite zeolite membranes, the cost of the support is one of the main factors to be consider, about 70% of the final cost [16]. Another issue to deal when ceramic substrates are used is the sealing, which could be expensive and unstable under operation conditions. Compare with ceramic supports, the synthesis of composite membranes on steel substrates allow the welding of the support and an easier ensemble to the permeation module. On the other hand, due to the noticeable differences in surface properties between stainless steel (SS) and zeolites, it is difficult to make zeolite layers grow well on the SS surface. Additionally, the SS support shows some drawbacks such as a high roughness of the surface and a large and wide pore size, which cause some problems during membrane synthesis. To solve these problems, it is necessary to develop adequate approaches to modify the support surface so as to make it suitable for zeolite layer growth.

The present work focused on the synthesis of thermally stable NaA zeolite membranes with low defect density on top of porous stainless steel tubes and disks. The optimization of seed size and seeding approach was performed using planar supports. In order to improve the quality of the zeolite layers, a concentrated gel was used to sustain nucleation and growth processes during the hydrothermal synthesis. The effect of the 3-aminopropyltriethoxysilane (APTES) modification of the support and the use of vacuum in the hydrothermal synthesis were analyzed. $H_2$, $N_2$, $CO_2$ and $CH_4$ single gas and mixture permeation measurements were performed as a function of temperature and pressure using tubular zeolite membranes.

## 2. Experimental

### 2.1. Conditioning of the support

Porous stainless steel 316 L (Mott Metallurgical Corporation) with two different geometries, disks and tubes were used as supports (grade 0.1 and 0.2 μm). Prior to the NaA zeolite layer deposition, the supports were washed with a basic solution (0.12 M $Na_3PO_4$. $12H_2O$, 0.6 M $Na_2CO_3$ and 1.12 M NaOH) in ultrasonic bath to remove organic pollutants and dirt at 373 K [17]. Then, the substrates were rinsed several times with deionized water and, later, in isopropyl alcohol for 15 min. Finally, the substrates were dried in an oven at 373 K for 3 h and then calcined at 773 K for 12 h.

### 2.2. Synthesis of seeds and seeding of the support

Three different suspensions of zeolite nuclei were tested for the seeding of the support:

- NaA crystals suspension (CS): prepared by suspending the NaA zeolite powder in water after being synthesized at 353 K with a concentration of 1.03 g/L.
- Synthesis gel AT24: a silicate solution and an aluminate solution were mixed obtaining a molar ratio of $1Al_2O_3$:$1.92SiO_2$:$3.16Na_2O$:$134H_2O$ and the resulting gel was aged for 24 h. Then the hydrothermal synthesis was carried out at 353 K for 8 h.
- Synthesis gel AT48: the same procedure employed for AT24 was used with an aging time of 48 h.

The support was seeded by vacuum-assisted immersion using a waterjet pump to generate a pressure difference between both sides of the support in order to ensure the plugging of the zeolite nuclei into the support pores and the surface coverage. The support connected to the vacuum system was immersed in the suspension for one minute and the process was repeated 4 times. Then, the support was dried in an oven at 353 K overnight.

### 2.3. Preparation of NaA zeolite membranes

NaA zeolite membranes were hydrothermally synthesized on the outer surface of tubular supports and on top of disk substrates using the secondary growth method. In order to prevent zeolite deposition on the bottom side of the disks, they were covered with teflon tape. Two precursor solutions were prepared separately, an aluminate solution and a silicate solution. The aluminate solution was prepared by dissolving 3.85 g of NaOH and 3.03 g of $Na_2Al_2O_4$ in 60 ml of deionized water. For the silicate solution, 1.78 g of silica powder (Aerosil 200) were dissolved in 26.70 mL of deionized water. Both solutions were immersed in a thermal bath at 363 K for 15 min. Then, the aluminate solution was added to the silicate solution to obtain a synthesis gel with a molar ratio of $1Al_2O_3$: $3.5SiO_2$: $8.4Na_2O$: $268H_2O$ [18]. Once the synthesis gel was homogenized, the stainless steel support was immersed in the synthesis gel and the hydrothermal synthesis (HS) was carried out at 363 K for 8 h under continuous agitation using the system previously described [18]. To improve the perm-selective properties of membranes, the hydrothermal synthesis stage was repeated until no $N_2$ flow was detected across the membrane without thermal treatment.

To study the effect of the vacuum on the quality of the membranes, two approaches were considered: i) the synthesis of the membrane by applying vacuum in all the stages, and ii) using vacuum only during the last hydrothermal deposition of zeolite.

### 2.4. Support modification with APTES

With the aim to improve both the adhesion between the zeolite layer and the substrate and the perm-selective properties, NaA membranes were synthesized with a further modification of the support. After oxidation and seeding, the support was treated with

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