Zeolite A-Carbon Membranes: Possibilities in H_2 Purification and how to Overcome their Shortcomings

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Abstract: This work describes the modification of zeolite Na-LTA membranes supported on macroporous carbon materials, prepared by a combination of secondary hydrothermal treatment followed by different alternative post-synthesis procedures, which aim at improving the permeance properties of the as-synthesized Na-LTA membranes with a simulated reformer mixture (H_2, CO, CO_2 and H_2O) towards their use in a hydrogen purification device.These post-synthetic treatments include the deposition of a thin layer of amorphous silica formed by the hydrolysis of a silicon alcoxide, the coating with a thin metallic film by electroless plating, and the deposition of noble metal nanoparticles. Our results indicate that some of these treatments, which may be performed very quickly compared to other treatments which are generally used in order to improve the quality of the membranes, result in membranes which may effectively separate H_2 from CO under simulated reformer conditions. Considering the simple approach employed in some of the cases described in this study, the potential benefits should be considered highly interesting in fields such as membrane recovery and membrane selectivity control.

Keywords: Zeolite, membranes, hydrogen purification, fuel cells.

1. INTRODUCTION

The development of zeolite membranes was first conceived as a means to overcome the problem of the high pressure drops that would result from using a zeolite bed, as Mintova and Valtchev pointed out [1]. In short, “condensing” the properties of a zeolite in an almost bidimensional layer constituted a substantial improvement from the first form of zeolite membrane that was reported by Suzuki [2]. After two decades of research and development and despite the fact that many significant advances have been made, the only zeolite membrane that has been used at a large plant scale was a NaA zeolite grown on an alumina support for the pervaporation of water-organic solvent mixtures [3]. The reason for this seemingly limited success could be that while for pervaporation applications strongly hydrophilic (or hydrophobic) membranes have shown great promise, separations of gases with similar characteristics (e.g. xylene isomers) require a degree of sophistication in the synthetic protocol that makes scaling-up very difficult [4].

Hydrogen fuel cells have become interesting candidates for the replacement of conventional power devices for mobile applications, especially since they overcome their mechanical and thermodynamic restrictions [5]. In this respect, hydrogen purification and separation have been identified as one of the main obstacles in the development of advanced hydrogen technologies [6]. In order to deliver a sufficiently pure hydrogen stream using a reformer (which is nowadays the most widespread alternative for hydrogen production [7]), zeolite membranes have been proposed as an interesting alternative due to their properties [8]. Considering the nature of the gases that need to be separated, zeolite A (LTA type structure) membranes have been selected as the potential candidates [9].

In this respect, our research group has already reported the usefulness of ion-exchanged zeolite LTA membranes supported on carbon materials for the separation of H_2/CO mixtures [10, 11]. Macroporous graphite materials are very attractive as zeolite membrane supports due to their exceptional thermal and chemical stability, tunable shape, porosity, hydrophobicity and surface chemistry, which confer them significant advantages when compared to metallic supports (which may be easily etched or corroded in the reaction media) and ceramic supports (which are expensive and brittle) [10, 12]. The behavior of the supported zeolite LTA membranes was fine-tuned by modulating the effective pore size of the zeolite by substituting the cation in the framework. It must be emphasized that the ion-exchange of Na^+ ions by Cs^+ ions in the as synthesized membranes Na-LTA/C materials was necessary to get high quality membranes for this application. That approach was simple and reproducible but the crystalline structure was partially distorted because a larger cation had to

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be accommodated into the zeolite network. In order to increase the applicability of said membranes, it would be useful to find other simple and reproducible protocols to fine-tune the zeolite effective pore size in the membranes Na-LTA/C which could moreover be applied in a reproducible way. In this study, we have performed a series of post-synthetic treatments on as-prepared Na-LTA/C composite materials in order to improve modify their performance:

i. Deposition of an amorphous silica layer by hydrolysis of a silicon alcoxide (i.e. passivation of the zeolite surface) [13]. (Sample Na-LTA/C-Si)

ii. Coating of the zeolite membrane surface by deposition of polymer-capped metal nanoparticles [14] (Sample NaA/C-Pd).

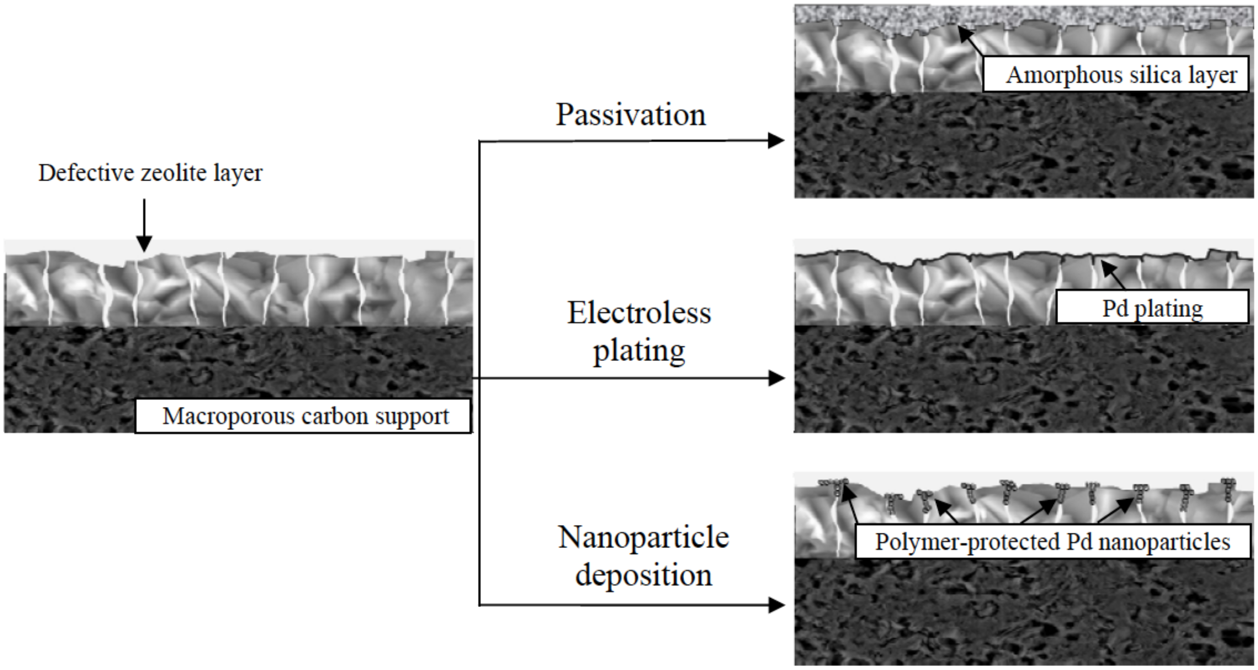
iii. Coating of the zeolite membrane surface by electroless plating [15, 16] (Sample NaA/C-PdSn).

Scheme **1** has a representation of these three different processes employed to produce high-quality membranes starting from Na-LTA zeolite membranes supported on a carbon material. The main aim of these post-synthetic treatments is to tune the zeolite effective pore size by coating the upper section of the zeolite film and to use them for hydrogen purification for PEM fuel cells (i.e. to obtain a purified hydrogen flow with a CO concentration lower that 10ppm under simulated reformer mixture containing 50% H_2, 1.25% CO, 20% of CO_2 in He and 5% H_2O).

2. EXPERIMENTAL

2.1. Zeolite Membrane (NaLTA/C) Synthesis

LTA/carbon membranes were prepared by the secondary growth following the methodology described in our previous works [10-12]. The carbon support, consisting of commercial macroporous carbon sheets (thickness = 0.3 mm, mean pore size 0.7 μm, geometric area 1.54 cm^2) provided by Poco Graphite (sample reference DFP-1), was cut into pieces and subjected to an oxidative treatment which consists in immersing the carbon pieces in boiling concentrated nitric acid for 12 hours in order to create surface oxygen groups. Then, the treated carbon support was seeded by means of Electrophoretic Deposition (EPD) [17] using a LTA colloidal suspension for 30 minutes [10-12]. The employed seeds were prepared by hydrothermal treatment using a synthesis solution with the following molar composition: $0.22Na_2O \cdot SiO_2 \cdot 1.0Al_2O_3 \cdot 8.0(TMA)_2O \cdot 400H_2O$, under hydrothermal conditions (synthesis temperature 336 K, reaction time 63 hours) [12]. Finally, a hydrothermal synthesis was carried out over the seeded support and a thin zeolite film was grown. The molar composition of this LTA synthesis solution was $50Na_2O \cdot 5.0SiO_2 \cdot 1.0Al_2O_3 \cdot 1000H_2O$ and the hydrothermal conditions were a



Scheme 1: Representation of the different mechanisms employed to produce high-quality membranes starting from Na-LTA zeolite membranes supported on a carbon material.

synthesis temperature of 373 K for 4.5 h. After hydrothermal treatment, the samples were sonicated for 15 minutes, washed with abundant water and dried overnight at 100ºC.

2.2. Zeolite Membrane Modification

2.2.1. Sample Na-LTA/C-Si Preparation

In order to coat the zeolite layer surface with an amorphous silica layer [13] with an estimated thickness of approximately 100 nm, three aliquots of 10 µL of a dilute solution of TEOS in EtOH (25µL TEOS/ 10ml EtOH) were deposited on the surface of the zeolite layer of several as-synthesized Na-LTA/C membranes. After the addition of each one of the aliquots, the membranes were introduced in an oven at 100ºC for 30 seconds to evaporate the solvent, which causes the precipitation of the silica upon hydrolysis of the silicon alcoxide.

2.2.2. Sample Na-LTA/C-Pd Preparation

A small volume (50 µL) of a suspension of Pd nanoparticles [14] in MeOH prepared with a concentration of 0.60 mg_{Pd}/mL was placed on the surface of the zeolite in 10 µL aliquots and the solvent was left to evaporate at 100ºC in an oven after each addition. This amounts for a total amount of metallic Palladium of 0.03 mg of Palladium deposited on the surface of the zeolite layer. Assuming a homogeneous deposition and taking into account the density of Palladium (12.023 $g\cdot cm^{-3}$), the estimated thickness of the deposited layer is 1.6 μm.

2.2.3. Sample Na-LTA/C-PdSn Preparation

The coating of the zeolite layer surface by electroless plating was performed in two steps. Two diluted acidic (pH=4) 5mM solutions were prepared, Pd (II) solution using $Pd(ac)_2$(SigmaAldrich) and Sn (II) solution using $SnCl_2\cdot H_2O$(SigmaAldrich). First, the zeolite Na-LTA surface was activated prior to the electroless plating by Pd-Sn redox reaction [15] in order to deposit Pd seeds which would favour the anchoring of the Pd plating film. This activation process involved immersion of the Na-LTA/C membranes in the Sn (II) solution for 5 minutes, followed by drying in air. Then the membranes were immersed in the Pd(II) solution for 5 min. The membranes were then washed by immersion for 5 minutes in deonized water. This process was repeated 5 times for each membrane. The second step is the electroless plating which was performed according to Ref. [16]. The Na-LTA/C membranes were immersed in a freshly prepared Pd (II) solution (0.01M, pH=8) and heated and equilibrated at 50ºC. The reducing agent, 5 mL of a NaH_2PO_2 solution (0.24 M), was added dropwise. After 30 minutes, the membranes were washed with abundant water and dried at 100ºC for 12 hours. According to the authors [16] this treatment results in a Pd-P coating with good adherence with a thickness of around 2 μm.

2.3. Membrane Characterization

The surface modification performed on the as prepared membranes was characterized by scanning electron microscopy (SEM) in a HITACHI S-300N microscope. Energy dispersive X-Ray spectrometry (EDX) was used to ascertain the chemical composition on the prepared membranes. Incident electron beam energies from 3 keV to 30 keV were used.

The permeation measurements were performed by duplicate to assess the reproducibility of the results in a Wicke-Kallenbach (WK) cell. Prior to all experiments, the membrane was out-gassed and dried by heating it at 423K for 6 hours under a constant He flow of 100 ml/min on both the feed and permeate side.

The permeation experiments were carried out at three different temperatures, 303, 398 and 423K, with a system pressure of 1 bar. Two different kinds of experiments were carried out to test the membrane permeation properties:

(i) Simulated reformer mixture on dry basis (50% H_2, 1.25 % CO and 20% of CO_2, balance He).

(ii) Simulated reformer mixture (50% H_2, 1.25 % CO, 20% of CO_2 and 5% H_2O, balance He).

The total flow rate for all experiments was 100 ml/min. The gases were swept with He (100 ml/min) at the permeate side and analyzed with a mass spectrometer (Balzer, Thermostar GSD 301T) and a gas chromatograph (Agilent Technologies 6890N equipped with a carbon-PLOT column operating at 303K and a TCD detector). The detection limit of this mass spectrometer is 1 ppm under the aforementioned conditions. For those samples where the CO permeance was below the detection limit of the mass spectrometer (i.e. permeances values of 0), additional measurements were carried out reducing the He flow rates to the minimum rate allowed (30 ml/min). From the permeation experiments, permeances were calculated considering the partial pressure difference between the retentate and permeate sides.

3. RESULTS AND DISCUSSION

3.1. Membrane Characterization

The samples were firstly screened by means of SEM to check the zeolite layer integrity, as we have reported previously [10, 11]. Figure **1** shows the SEM images corresponding to the modified membranes with the different post-synthetic treatments (SEM images of the as-synthesized Na-LTA/C membrane are also included for comparison purposes).

Figure **1A** shows the top view of the as-synthesized (untreated) Na-LTA/C membrane, where it can be seen that the macroporous carbon graphite support is completely covered with a homogeneous and continuous zeolite layer, which has anestimated zeolite layer thickness of 2-3 µm, as it was reported in our previous study [10]. At this point, it is noteworthy to mention that the zeolite layer is formed exclusively by LTA crystals as it was confirmed by XRD analysis [10].

Comparing Figure **1A** (Na-LTA/C) and 1B (Na-LTA/C-Si), it becomes evident that sample Na-LTA/C-Si shows a surface with a marked decrease in the number of visible grain boundaries or crystalline edges compared to the as-prepared sample. This observation is explained on the basis that the SiO_2 layer deposited coats the entire membrane surface, and given its amorphous nature, the outlook of the material surface appears less dominated by the presence of grain boundaries than the as-synthesized Na-LTA/C membrane. Thus the top-view of the sample shows a well intergrown zeolite layer which is coated by a layer of what would appear as uncrystallized gel (as if the sample had undergone an incomplete hydrothermal treatment, as we have previously reported [17]).The electroless plating treatment applied on sample Na-LTA/C-PdSn resulted in an amorphous layer that covered the entire zeolite surface. This newly formed layer had large cracks on its surface, of approximately 1 µm in size which is a marked difference with the results reported in [16] in which a continuous Pd-based layer is obtained. Nevertheless, this occurrence did not hinder the membrane permeation properties of the prepared material (see below). On the other hand, sample Na-LTA/C-Pd did not show any significant differences compared to the as-synthesized material (results not shown). This may be explained on the basis that the average polymer capped Pd nanoparticle size (approximately 2.2±0.5nm) [14] is beyond the spatial resolution of the SEM equipment used. In this case, the surface landscape of the zeolitic material is

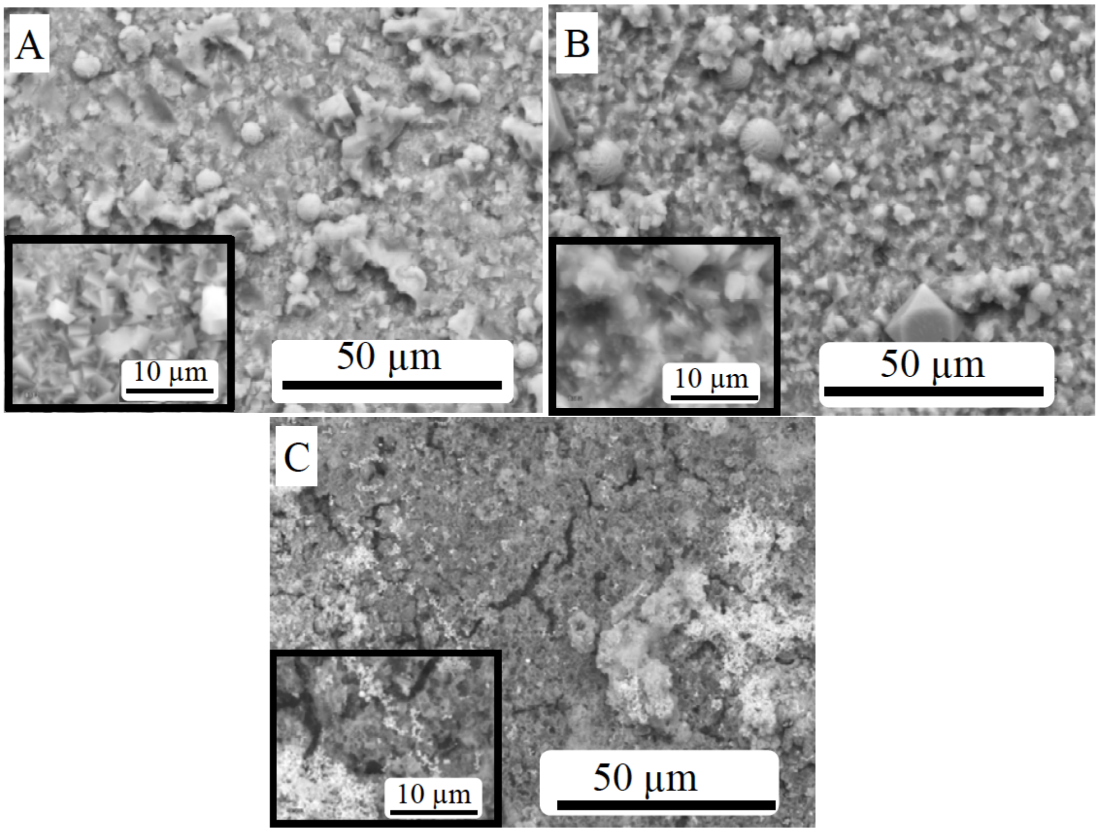


Figure 1: SEM images of the prepared samples (**A**) Na-LTA/C, (**B**) Na-LTA/C-Si, (**C**) Na-LTA/C-PdSn.

clearly dominated by the presence of intergrown Na-LTA crystals, identical to the SEM images shown in Figure **1A**. This result, however, contrasts with the fact that the deposited Palladium layer should be visible in the SEM considering the aforementioned estimated thickness (over 1.5 μm). This may indicate that a large fraction of the deposited Pd nanoparticles may be sealing the cracks and defects in the zeolite layer, which would be numerous (and most probably run along the whole zeolite layer depth).

The surface composition of the prepared samples was analyzed by means of EDX (see Figure **2**) in order to determine the effect of the different surface treatments on the surface composition of the post-treated membranes. Figure **2A** shows the EDX corresponding to the original Na-LTA/C membrane. In the case of the Na-LTA/C-Si (results not shown), while a modification of the Si/Al ratio was expected due to the presence of the thin silica film, no appreciable changes were observed. This was due to the thin cross-section of the amorphous silica film which was not enough to cause any appreciable modification of the Si/Al ratio upon EDX measurement.

The sample showing the most noticeable surface composition difference from the EDX analysis was Na-LTA/C-PdSn (See Figure **2B**), in which a very strong signal due to Pd was observed. In this sample the Sn/Pd treatment [15] increases the stability of the final Pd layer formed by seeding the surface with Pd nuclei (which help towards the anchoring of the Pd layer) prior to the electroplating step. According to Yeung *et al*. [15], the surface activation by Pd/Sn produces a better fixation of the Pd layer on the zeolite layer, giving a higher mechanical stability over time because it prevents the flaking-off and separation of the Pd layer from the zeolite layer surface. It must be noted that the presence of P in the sample is justified by the formation of Pd-P alloy phases due to the electroless plating procedure followed [16]. However, the presence of a significant amount of Sn on the sample detected by EDX analyses revealed that Tin (IV) oxide deposits

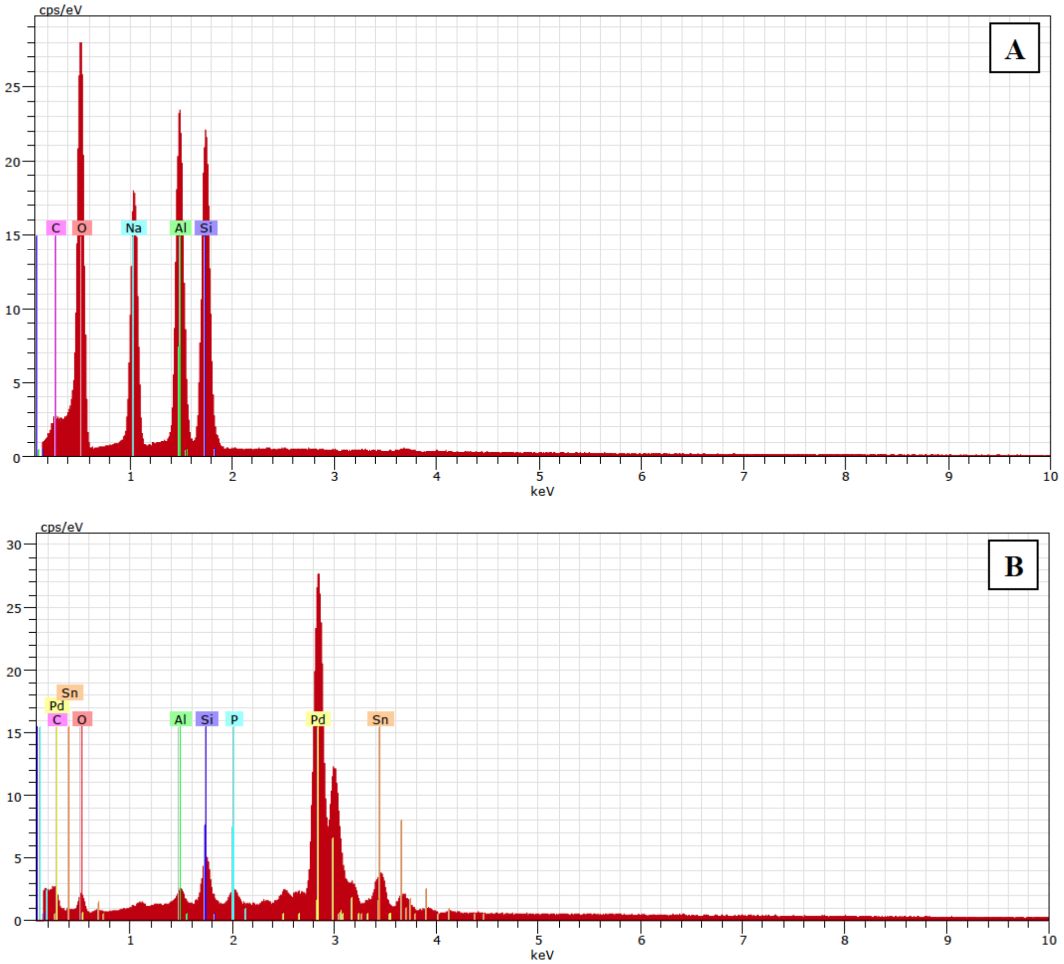


Figure 2: Energy-Dispersive X-ray spectrometry (EDX) analysis corresponding to: (**A**) as synthesized Na-LTA/C membrane; and (**B**) Na-LTA/C-PdSn.

remained on the zeolite layer surface despite the thorough washing with water. The detection of Sn species also serves as an indication that the deposited Pd-based layer is indeed within the expected value (≈2 μm), for the penetration of the X-Ray probe ranges between 2 and 6 μm for acceleration voltages of 5 and 20 kV, respectively.

3.2. Membrane Permeation Properties in a Simulated Reformer Mixture on Dry Basis

Preliminary permeation tests in a simulated reformer mixture on dry basis are necessary to determine the usefulness of the modified Na-LTA/C materials. Figure **3** summarizes the permeance results of the modified membranes and the untreated Na – LTA/C membrane. All permeance values include the error bars for each measurement taken from three different samples.

Bearing in mind that the main objective is reaching a purified H_2 flow with a CO concentration lower than 10 ppm, it is possible to screen the membranes after testing them in dry conditions. From Figure **3**, it became apparent that all the membranes are modified in one way or another by all of the approaches developed, and thus their membrane performance is affected.

Analyzing H_2 permeation properties (see Figure **3A**) and taking into consideration its small size, very low polarizability and high diffusivity [11], it is expected that the H_2 permeance should not be affected to a large extent by any of the treatments. In this sense, Na-LTA/C-Pd and Na-LTA/C-Si were the membranes prepared with the least aggressive modification methods. In these two samples H_2 permeation properties were not affected to an appreciable degree. On the contrary, H_2 permeation was considerably modified in the Na-LTA/C-SnPd materials. Considering that the plating procedure is the method involving the harshest chemical conditions in terms of pH and temperature performed on the membranes, the high permeance flux could be attributed to a possible modification of the separation layer. In this respect, another possible explanation might be that deposition of the Pd layer (a well-known selective H_2 membrane) enhances H_2 permeation, which would explain why hydrogen permeance is affected to a much more significant degree than CO (Figure **3B**) or CO_2 (Figure **S1**).

Focusing on the CO permeation properties (see Figure **3B**), the composite Na-LTA/C-Pd is not suitable for H_2 purification, because CO permeates through the membrane. These results indicate that the presence of Palladium nanoparticles on the membrane surface does not hinder CO permeation sufficiently, which makes this treatment not useful to obtain efficient membranes for H_2purification.

At this moment, the influence of the CO_2 and CO-zeolite interaction on CO permeation through the membrane must be pointed out. Sea *et al.* [18] suggested that CO_2 molecules are adsorbed on the external surface of the pores and then migrate into the pores by surface diffusion. These adsorbed molecules reduce the openings of the micropores by translation-collision mechanism. In our previous study [11], based on experimental studies, we determined that the CO_2 molecules produce two effects: (i) inhibition of CO adsorption on the surface and pores due to the competitive adsorption between CO and CO_2 and (ii) the adsorbed molecules reduce the openings of

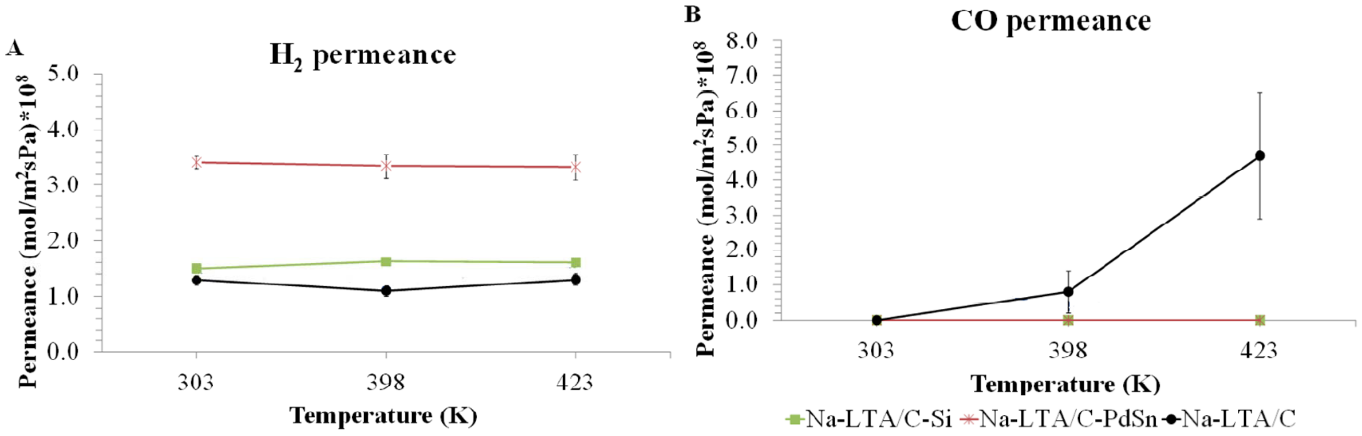


Figure 3: Permeances of different gases (**A**) H_2, (**B**) CO in a $H_2/CO/CO_2$ mixture at different temperatures on dry basis in as-synthesized and modified Na-LTA/C membranes.

micropores. However, this effect is drastically reduced as the temperature increases and CO permeates through the untreated Na-LTA/C membrane (see Figure **3B**) at 423K with high flows. Then, the post-synthetic treatments are necessary in order to use this kind of membranes at higher temperatures.

Comparing the results in Figure **3B**, the main consequence of the use of a post-synthetic treatment is that the CO permeation at the three temperatures studied is completely hindered (no CO permeation detected using Mass Spectrometry) in the Na-LTA/C-Si and Na-LTA/C-PdSn materials. These experiments using a simulated reformer mixture in dry basis are suggesting a great potential in hydrogen purification in the exhaust coming from a reformer unit for the Na-LTA/C-Si and Na-LTA/C-PdSn materials. Electroless plating is a popular technique for preparing thin Pd film over a support [15, 16] (in our case a zeolite membrane) which are highly selective to H_2 permeation. Thus, it is expected that this film may act as a diffusion barrier to inhibit the CO permeation through the prepared material (Na-LTA/C-PdSn) as our observed CO permeance is reduced to zero.

In the case of LTA/C-Si, the deposition of silica on the surface (Na-LTA/C-Si) may have changed the openings of the Na-LTA pore zeolite membrane and as a result, CO molecules cannot permeate through the membrane at all the temperatures under study, while the H_2 permeation is similar due to the H_2 molecules being able to diffuse trough the six-member rings in the sodalite (β-cages) [19] and the eight member ring of the α-super cages, as we concluded in our previous study [11]. A similar approach of fine tuning the porosity was previously done by Kim *et al*. [20], who prepared silica membranes supported on porous alumina, and demonstrated that the silica layer permitted the separation of small molecules such as H_2, CO_2 or N_2, by a molecular sieving effect. Moreover, Lee *et al.* [21] prepared silica membranes and studied the effect of the Si deposition time on the final permeation properties of mixtures containing H_2, CO, CO_2 and CH_4. It was observed that the selectivity to H_2 increases with the synthesis time and the permeation of the other gases decreased and gave them evidence that the mechanism of molecular differentiation by the silica layer is through size selectivity. Finally, Hong *et al.* [22] used the catalytic cracking deposition methodololgy to effectively reduce the pore size of MFI/α-Al_2O_3 zeolite membranes to study the permeation of H_2/CO_2 single gas components and mixtures, observing this molecular sieve effect of the silica layer.

3.3. Membrane Permeation Properties in a Simulated Reformer Mixture

Figure **4** contains the permeation properties of the selected modified membranes (Na-LTA/C-Si and Na-LTA/C-SnPd) and the untreated material (Na-LTA/C) under humid conditions using a simulated reformer mixture (50%H_2, 1.25%CO, 20% CO_2 and 5% H_2O).When the Na-LTA/C membranes were tested under gas stream simulating the exhaust of a reformer, the presence of a very high concentration of moisture (5%) in the feed stream resulted in CO permeance values which ranged from 4.8 to $2.9{\cdot}10^{-8}{\cdot}mol/m^2{\cdot}s{\cdot}Pa$. Based on our previous study [11], the permeation enhanced with the presence of H_2O in the feed stream corresponds to the interaction of the CO molecules with the zeolite (C-bonded) or with water (H-bonded). This possibility was hypothesized due to the strong interaction between zeolite NaA and water [23]. Taking into account the high hydrophilic character of zeolite Na-LTA, which arises from its low silica/alumina ratio, water may condense on the surface of the zeolite layer, thus providing an alternative pathway for the diffusion of CO through the membrane, which may be explained in terms of solubilisation of CO in the adsorbed water layer, thus greatly hindering the potential of these membranes (Na-LTA/C membranes).

The surface treatments to which the as-synthesized composites were submitted modified the membrane performance of the prepared samples by covering the zeolite coating with a layer of a substance of different chemical nature. These prepared materials have caused significant changes on the permeance properties of all the gases under study (H_2, CO and CO_2), and the main difference corresponds to the CO permeation. From the results shown in Figure **4B**, the membranes prepared by passivation (Na-LTA/C-Si) and electroless plating (Na-LTA/C-PdSn), showed a reduced CO permeationat 303K.No CO was not detected at high temperatures (398K and 423K) on the permeate side of the membrane, which constitutes a substantial advancement compared to the as-synthesized membrane.

In Figure **4A** it can be seen that the Na-LTA/C-PdSn material shows H_2 permeance values which are almost 3 times higher than those obtained for H_2 in our best

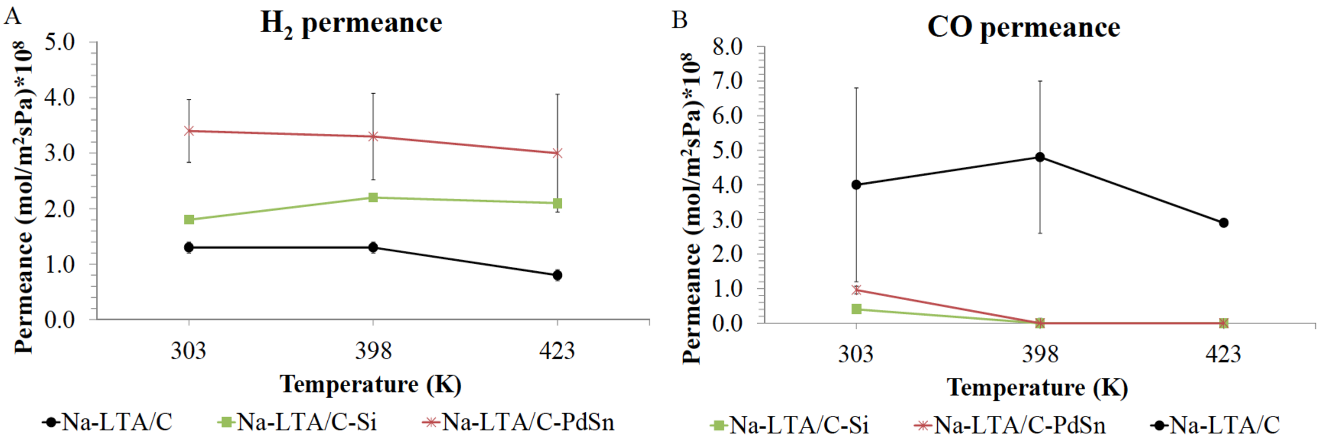


Figure 4: Permeances of different gases (**A**) H_2, (**B**) CO in a $H_2/CO/CO_2$ mixture at different temperatures on humid basis (simulated reformer conditions) in as-synthesized and modified Na-LTA/C membranes.

result reported to date (Cs-LTA/C) [11]. Furthermore, no CO permeationis detected at the outlet of the membrane at 423K (Figure **4B**). However, as mentioned before, plating methodology is considered a relatively aggressive treatment that could alter the zeolite membrane properties to a large extent. Moreover, Khatib and Oyama [24] observed that the presence of H_2 at temperatures below 573K produces different hydrides in Pd-based membranes, that deteriorates the mechanical properties of these kind of membranes and therefore, it could be the case that the Na-LTA/C-PdSn membranes would be deteriorated upon usage.

Focusing on the permeation results of the passivated material (Na-LTA/C-Si), the resulting membrane shows excellent H_2/CO separation properties at 398 and 423K. At 303K, despite the fact that CO permeation dropped from $4.0 \cdot 10^{-8}$mol/m$^2 \cdot$s$\cdot$Pa in the as-synthesized membrane to $0.4 \cdot 10^{-8}$mol/m$^2 \cdot$s$\cdot$Pa, being the H_2/CO separation factor of 4.5, the aim of the present work (to completely suppress the CO flow through the membrane) was only achieved at temperatures higher than 303K. This change in selectivity at all temperatures tested might be explained on the grounds that thin silica layers deposited on the external surface of zeolite crystals is a pore-engineering technique that has been used for the discrimination of the catalytic activity of the inner surface of zeolites from that of the external surface [13]. In this respect, the modification of the pore size by the interaction/condensations of the alkylsilane and the silanol groups of the surface of the zeolite renders a pore size which can effectively impede the diffusion of CO (molecular size 3.4 Å), while H_2 (molecular size 2.4 Å) diffuses at an enhanced rate at temperatures over 303K.

The results point out that passivation of the zeolite surface with an amorphous silica layer is an effective way to modify zeolite membranes supported on carbon materials, allowing us to improve their permeation properties up to the point of being able to purify H_2 even in the presence of high concentrations of CO_2 (20%) and water (5%) in the feed stream. Thus, sample Na-LTA/C-Si should be considered as a highly promising material for hydrogen purification at temperatures around 373-423 K, bearing in mind that the gases from the reformer goes out at 473 K and the PEM fuel cell operates at 353 K [25].

Hydrogen purification is a research topic which has been attracting significant attention during the past few years, being perhaps the best indicator the wide range of materials which have been reported in recent years for their use as membranes for this particular application. In this respect, some of the reported results deal with the separation of H_2 from CO_2, but the materials show enough promise to test them under similar conditions as those reported in our study. Chung *et al.* [26] reported a polymer composite hollow fiber which shows promising H_2/CO_2 separation factors. From a more applied perspective, Lambrecht *et al*. [27] and Tsotsis *et al*. [28] have reported the use of a commercial membrane and carbon sieve membrane for H_2 purification from syngas, respectively. Concerning the separation of H_2 from CO, several materials have been reported (and theorized) in recent years, markedly different from the "traditional" Pd-based membranes which nevertheless are still undergoing intense research to obtain ultrapure hydrogen [29]. Concerning the specific separation of H_2 of CO, Scott *et al*. [30] reported the use of a silicon nitride membrane which could completely block CO permeation from the feed stream, although permeance values are not reported. Other studies have reported hydrogen purification in gas streams consisting mainly of H_2 and CO_2, in which CO and steam were used as probes to test membrane performance [31, 32]. It must be noted that even in the case of the porous membrane [31] (a zeolite imidazolate framework-based membrane) no information is given concerning CO permeation, which is a critical issue for fuel cell membrane development. In this respect, some authors have hinted at the possibility of using MOF-based membranes for the purification of hydrogen, but, to the best of our knowledge, no results have been hitherto reported.

Taking into consideration all the aforementioned materials, it should be said that, the passivation of the zeolite surface with a layer of amorphous silica carried out in the present work is a very simple and reproducible approach, and requires very little time for its application, but also an amount or reagents which is close to negligible (0.075 µL of TEOS and 30 µL of EtOH per membrane).

Finally, the relevance derived from the use of a macroporous and hydrophobic support, which does not affect permeation through the membrane, opens up the possibility of analyzing the effect of the aforementioned treatments in the membrane properties of the synthesized materials.

As it has been mentioned in the introduction, the use of macroporous graphite discs is very attractive as zeolite membrane supports. In this respect, the use of a markedly hydrophobic support poses a new perspective towards understanding how water and other components affect membrane properties. When a meso-macroporous hydrophilic support is used, water may condense not only on the separation layer, but also in the smaller cavities of the support, which gives rise to variations in the fluxes of certain species, although that may in turn prove beneficial for certain gas mixtures. This capillary condensation, however, can be discarded when a macroporous carbon material is used, and as a result, permeation fluxes are only affected by condensation of water on the zeolitic pores. This provides us with an opportunity to analyze the membrane properties of the prepared materials from a more fundamental point of view. Our results indicate that water adsorption on the separation layer has an influence on the permeation flows of the different species involved, since at room temperature CO was detected for all the studied membranes. At temperatures above 303K no CO was detected in the case of samples Na-LTA/C-PdSn and Na-LTA/C-Si, which indicates that these two treatments can block the porosity responsible for CO permeation, even when the permeation tests are run under humid conditions.

4. CONCLUSIONS

We have shown different ways to modify LTA zeolite-based membranes supported on carbon materials which, being simple and reproducible, allow to improve their permeation properties up to the point of being able to purify H_2 even in the presence of high concentrations of CO_2 (20%) and water (5%) in the feed stream. The relevance of the use of a macroporous and hydrophobic support, which does not affect permeation through the membrane, opens the possibility of analyzing the effect of the aforementioned treatments in the membrane properties of the synthesized materials.

Pore size engineering performed by the deposition of an amorphous silica layer renders a high-quality membrane which can effectively discriminate H_2 from CO at temperatures higher than ambient. It should also be mentioned that of all the described methodologies, passivation of the surface is not only simple and requires very little time for its application, but also an amount or reagents which is close to negligible, making it an economically viable alternative for the preparation of hydrogen purification devices.

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SUPPLEMENTAL INFORMATION

The supplemental materials can be downloaded from the journal website along with the article.

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