

Tesi doctoral presentada per En/Na

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amb el títol

**"Preparation, characterization and modeling of zeolite NaA membranes for the pervaporation dehydration of alcohol mixtures"**

per a l'obtenció del títol de Doctor/a en

QUÍMICA

Barcelona, 29 de maig del 2006

Facultat de Química  
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The list of results obtained in this work lead to the following conclusions:

1. New methods for the reproducible preparation of composite zeolite NaA membranes on the outer- and inner side surface of tubular  $\alpha$ -alumina and titania (rutile) by means of the secondary growth method have been presented and thoroughly discussed in chapter IV. This method relies on decoupling the nucleation and growth steps by hydrothermal synthesis.
  - 1.1. A cross-flow filtration seeding technique (*dynamic seeding*) has been presented in this chapter to allow a controlled and uniform seeding of zeolite NaA particles from a suspension on the inner side of porous tubular supports. Among the operational variables of the process, the feed flow rate, transmembrane pressure and pH play a relevant role in the final seeding weight gain values after seeding (SWG). This seeding technique strongly improves the quality of the synthesized membranes in the growth step for the experimental synthesis methods that involve low renewal of the synthesis gel.
  - 1.2. The synthesis methods surveyed in this chapter include batchwise synthesis in an open vessel, synthesis under the action of a centrifugal field, semi-continuous synthesis system and continuous synthesis system. The two latter methods allow to obtain zeolite layers with a lower amount of large defects (fissures and cracks) and with  $N_2$  permeances in the range  $10^{-9}$ - $10^{-8}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>. This order of magnitude for  $N_2$  permeance reveals as necessary for the synthesis of good quality zeolite NaA membranes. On the other hand, the inner-side membranes show good quality for weight gains after synthesis using the semi-continuous synthesis method around 9-10 mg cm<sup>-2</sup> of zeolite material, which is the half of that required for the synthesis of good quality outer-side zeolite NaA membranes.
  - 1.3. The membranes have been characterized by single gas gas permeance, PV of ethanol/water liquid mixtures, XRD, SEM and EDS. Table IV.8 summarizes the seeding and synthesis conditions for the membranes synthesized in this work that show the best reproducibility, together with the water/ethanol selectivities that can be reached. The inner-side membranes prepared onto titania supports using the continuous synthesis system in only 1 synthesis cycle with a preliminary brush-seeding step show the best PV performance for the dehydration of ethanol/water mixtures, since this method allows a continuous renewal of the gel in the lumen of the tubular supports. The highest water/ethanol selectivities achieved in this work are >10000 with total fluxes up to 0.84 kg m<sup>-2</sup> h<sup>-1</sup> for a feed composition 92 : 8 wt.% (ethanol : water) at 323 K and for a permeate vapor pressure <2 mbar. The selectivities obtained in this work approach the best values reported in the literature for flat and outer-side tubular zeolite NaA membranes.

2. Some of the zeolite NaA membranes synthesized in this work have been applied in chapter V to the dehydration of binary alcohol/water (alcohol: ethanol, 1-propanol, 1-butanol y 1-pentanol) and ternary liquid mixtures (1-pentanol/water/DNPE) by VPV (see chapters V.1 and V.2). Linear ethers such as DNPE do not pervaporate across these membranes. The temperature and water composition in the feed exerts a positive effect in the total flux through the membranes with a maximum in the selectivity for a water composition ca. 20 mol% (10 wt.%), while the permeate vapor pressure exerts a negative effect in the dehydrating ability of the membranes. Furthermore, for a given membrane, the selectivity towards the dehydration of primary alcohols tends to increase with the length of chain of the alcohol due to its increased hydrophobic character and size. Using experimental separation and kinetic data, a multitubular zeolite NaA membrane reactor has been simulated in chapter V.3 to carry out the liquid-phase etherification reaction of 1-pentanol to di-n-pentyl ether (DNPE) catalyzed by a sulfonated resin. In a preliminary approach, this chapter points out the possibility to improve the conversion of the reactor in comparison with a conventional multitubular fixed-bed reactor due to the selective water removal by the membrane, which might enhance the activity of the catalyst and thus the kinetics of the reaction in the reactor. Further research in this field might involve the run of a future laboratory-scale plant to carry out etherification reactions by means of zeolite NaA membrane reactors.
3. A mathematical model has been presented and experimentally validated in chapter VI.1 to predict pore size distributions (PSDs) in meso- and macroporous membranes for UF, NF and MF applications using moment theory. The method allows the characterization of membranes in terms of PSDs instead of the traditional characterization by molecular weight cutoff values (MWCO) by performing three permeation experiments: (1) pure Knudsen N<sub>2</sub> permeance, (2) pure water permeability, and (3) non-hindered diffusion of an electrolyte. The method allows to overcome the shortcomings related to low sample representativity of microscopic techniques (e.g., SEM, TEM, FESEM and AFM). On the other hand, the method also allows to distinguish between dead-end pores and active pores to permeation, which cannot be usually distinguished by techniques such as permoporometry and mercury porosimetry. Finally, compared to the latter two characterization techniques, the method does not involve the use of the Kelvin equation, which shows strong limitation for pores <5-10 nm. Therefore, pores in this range and even lower, in the nearby of the micropore zone (2-10 nm) can be also in principle subjected to characterization by the present method.
4. The latter method used for characterization of meso- and macroporous membranes has been extended in chapter VI.2 to characterize large defects in zeolite NaA layers in the meso- and macroporous range. This chapter has proven that such defects can be

characterized by a collection of VPV experiments for the separation of ethanol/water mixtures at feed (retentate) pressures in the range 1-8 bar. Structural information concerning large pores in zeolite NaA layers can be obtained from the intercept and slope of the curve that describes the evolution of the total flux permeated through a zeolite NaA membrane with the liquid feed pressure. The main conclusion derived in chapter VI.2 is that the zeolite NaA membranes synthesized in our laboratory lose partially their separation ability to dehydrate ethanol/water liquid mixtures for intercrystalline porosities  $>10^{-3}$  [-]. Moreover, although a zeolite membrane shows good PV performance towards the dehydration of organic mixtures, the presence of a small number of meso- and macroporous defects in the zeolite layer cannot be ruled out, which might cause a reduction of the selectivity of the membranes from the theoretical value of  $\infty$  that would be in principle expected.

5. A new isotherm based on general concepts in solution thermodynamics (3D), namely the *Potential Thermodynamic Isotherm* (PTI), has been developed in chapter VII.2 to account for the adsorption equilibrium of gases and vapors in microporous materials (e.g., active carbons and zeolites), which involves a potential trend between the free energy relative to saturation,  $-\Psi/RT$ , and the variable  $Z=1/-\ln(\Pi)$ , where  $\Pi = P/P^0$  is the reduced pressure,  $\theta$  is the fractional loading of the surface [-] and  $m$  is a structural parameter of the adsorbent. This formulation is attractive because it allows to obtain structural information in microporous materials from the adsorption isotherm of  $N_2$  at 77 K, which might be later used to predict their ability to adsorb other gases and vapors (e.g.,  $H_2$ ). In light of the results shown in this chapter, microporous materials can be characterized from the adsorption isotherm of  $N_2$  at 77 K using the PTI. It should be noted that parameter  $m$  obtained from the fittings to the PTI might be useful for the prediction of the behavior of microporous materials towards the adsorption of gases and vapors (e.g.,  $H_2$ ).
6. In the same chapter it has been shown that the Dubinin-Astakhov isotherm, traditionally proposed to account for the adsorption of light gases in microporous materials, can be deduced from the PTI. However, according to the present formulation, the single-site Langmuir isotherm shows no correspondence with the TPI, which supports the idea that surface thermodynamics (2D) does not seem to be proper for the characterization of the adsorption behavior of microporous materials. Otherwise, this latter isotherm constitutes a good tool for the phenomenological description of the unary adsorption equilibrium of water and ethanol vapors in zeolite NaA powder according to the fittings that have been presented in chapter VII.1. This latter formalism can be extended to the equilibrium adsorption of binary mixtures using the PRAST theory.

7. According to the results presented in chapter VIII.3, the generalized Maxwell-Stefan (GMS) diffusional theory in its improved version and for weak confinement provides a good basis for the description of the VPV process in zeolite NaA membranes towards the dehydration of ethanol/water liquid mixtures. The fitted MS surface diffusivities at zero coverage at 323 K show values in the range  $2.37\text{-}4.90 \times 10^{-12}$  and  $1.94 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ , respectively, for water and ethanol (see Table VIII.8), which are lower than those obtained in the preliminary modeling shown in chapter VIII.2. The lower values for MS surface diffusivities at zero coverage observed for water than for ethanol might be again ascribed to size differences between both molecules.
  
8. MS surfaced diffusivities of water and ethanol have been also determined in chapter VIII.1 from experimental kinetic adsorption data on zeolite NaA powder obtained both in the microbalance and from breakthrough curve analysis. The values obtained for these diffusivities are 3-4 orders of magnitude lower than those obtained from the modeling of the VPV process through zeolite NaA membranes, which might be explained on the grounds of the contribution of grain boundaries of nanoscopic size defined between adjacent zeolite NaA crystals to the overall mass transfer across the zeolite membranes. Assuming that mass transfer through grain boundaries is governed by surface diffusion, both these pores and intracrystalline zeolite pores might contribute to the overall mass transfer as a global ensemble. However, since the size of grain boundaries is higher than the window openings in the  $\alpha$ -cages, the diffusion process across the former might be less impelled, that is, they might behave as fast diffusion paths due to the anisotropy of the zeolite layers. This anisotropy might be responsible for the higher apparent values observed for MS surface diffusivities.