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"

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This thesis is aimed at providing a new insight into the emerging field of synthesis and characterization of zeolite membranes able to carry out the separation of mixtures of industrial interest by pervaporation (PV). Much attention has been also given to modeling the PV process in zeolite membranes. To this end, an insight into the thermodynamics of adsorption equilibrium in micropores is provided and a method to characterize large defects in zeolite layers is also presented in this work. The main contributions in this thesis are shown and discussed along the forthcoming chapter of results (chapters IV-VIII) (see Figure II.1), which in its turn has been divided into five chapters without taking into account chapter III, that includes the description of all the experimental set up and procedures:

- Chapter IV: This chapter deals with the preparation of composite outer- and inner-side tubular zeolite NaA membranes by direct *in situ* and *ex situ* (secondary growth) hydrothermal synthesis. For the preparation of the latter, a cross-flow filtration technique is presented to allow a controlled and uniform seeding of zeolite NaA crystals from a suspension. Renewal of the gel can be achieved by means of three experimental systems: synthesis under a centrifugal field, semi-continuous synthesis system, and continuous synthesis system. The membranes have been characterized by N_2, He and SF_6 single gas permeance, pervaporation of ethanol/water mixtures, XRD and SEM/EDS. The effect of the synthesis conditions in the PV performance of the *as*-synthesized membranes is also discussed.

- Chapter V: This chapter shows the effect of the main operational conditions (feed and permeate pressures, feed composition and temperature) in the dehydration performance of *as*-synthesized zeolite NaA membranes by pervaporation. Some results concerning the pervaporation performance towards the dehydration of short- and long-chain alcohol/water binary and ternary mixtures are also shown and discussed. Finally, in light of this latter results and of some kinetic data obtained in our laboratory, a tubular zeolite NaA membrane reactor is simulated to carry out the liquid-phase etherification reaction of 1-pentanol to DNPE catalyzed by a sulfonated resin.

- Chapter VI: This chapter presents a new method to characterize pore size distributions (PSDs) in UF, NF and MF porous membranes from flux measurements by applying moment theory, which is validated with experimental data obtained in our laboratory. The method is extended to characterize large defects (i.e. meso- and macroporous) in zeolite NaA layers from VPV measurements, which allows the determination of a mean pore size and the intercrystalline porosity, which reveals as a valuable tool for directing synthesis strategies in the preparation of zeolite membranes.

- Chapter VII: This chapter presents the experimental results concerning unary and binary adsorption isotherms of water and ethanol vapors on zeolite NaA commercial powder. Several phenomenological isotherm models have been fitted to the experimental results. Moreover, the IAST and PRAST models have been used to predict binary water/ethanol adsorption isotherms. A new concept of ***Potential Thermodynamic Isotherms*** is also provided to describe the adsorption equilibrium of gases and vapors on microporous materials (e.g. active carbons and zeolites) from the adsorption isotherm of N_2 at 77 K by applying solution thermodynamics.

- Chapter VIII: This chapter is devoted to modeling the VPV process in zeolite NaA membranes towards the dehydration of ethanol/water mixtures. The adsorption equilibrium at the feed/membrane and permeate/membrane surfaces is modeled by (1) and Extended Langmuir adsorption isotherm, and (2) the Ideal Adsorbed Solution Theory (IAST) and Predictive Real Adsorbed Solution Theory (PRAST) from the unary adsorption equilibria models fitted to experimental data and discussed in chapter VII. The role of nanscopic defects or grain boundaries as fast diffusion paths is thoroughly discussed.

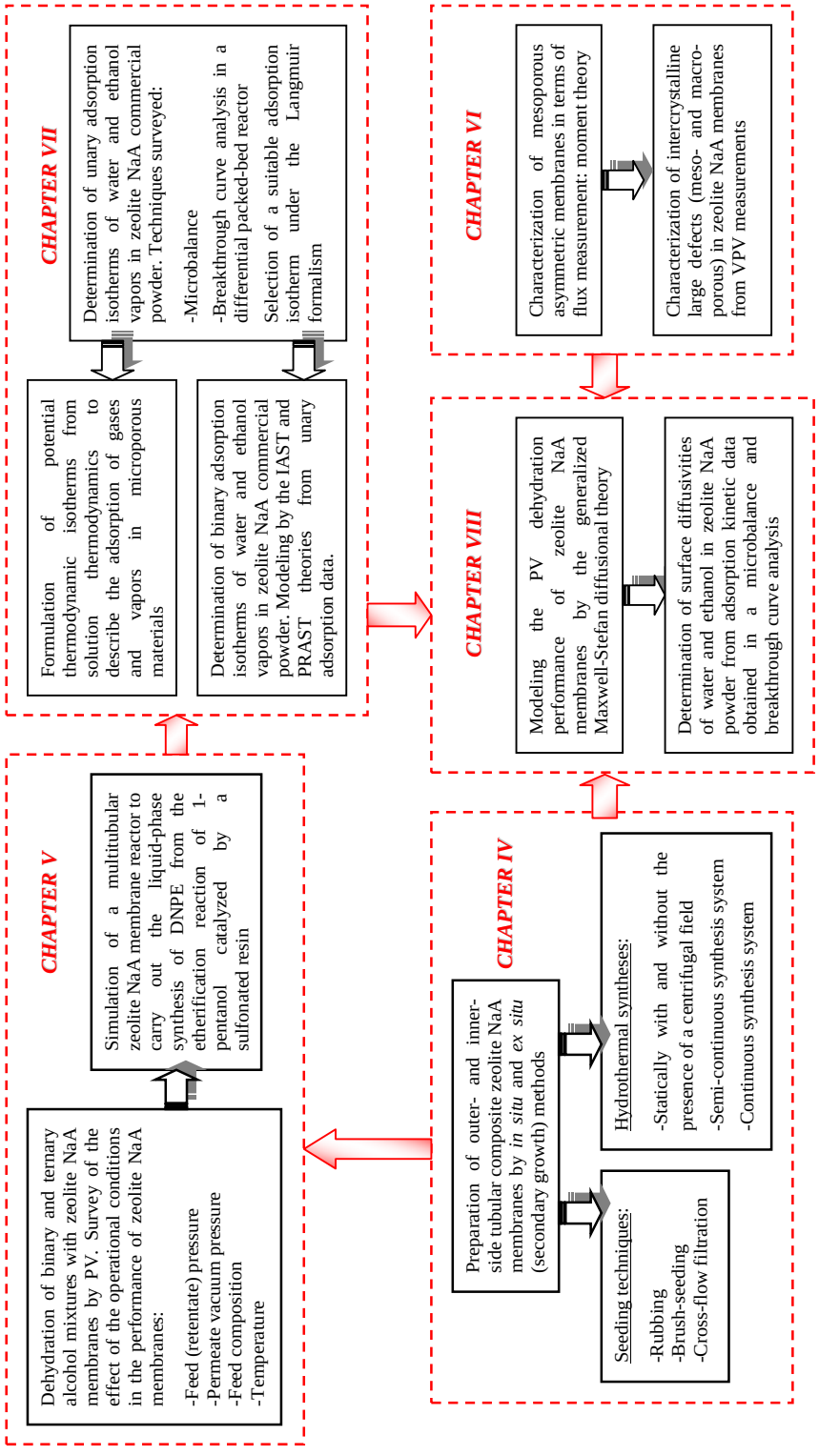

Figure II.1: Contents of the thesis