

Tesi doctoral presentada per En/Na

Marc PERA TITUS

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
Departament d'Enginyeria Química



UNIVERSITAT DE BARCELONA



I. INTRODUCTION	1
I.1. INTRODUCTION TO MEMBRANE SEPARATION.....	3
I.2. INTRODUCTION TO INORGANIC MEMBRANES.....	4
I.2.1. Classification of inorganic membranes	5
I.2.1.1. Dense membranes	6
I.2.1.2. Porous membranes	7
I.2.2. Mass transfer mechanisms in inorganic membranes	7
I.2.3. Characterization of pore size and pore size distributions (PSD) in meso- and macroporous membranes: an overview	10
I.2.4. Pervaporation	16
I.2.4.1. General concepts.....	16
I.2.4.2. Pervaporation with polymeric membranes.....	16
I.2.4.3. Pervaporation vs. distillation	17
I.3. ZEOLITES	18
I.3.1. Framework structure	18
I.3.2. Physical and chemical properties of zeolites	19
I.3.3. Zeolite NaA	22
I.3.4. Preparation of zeolites	23
I.3.5. Applications of zeolites	25
I.3.6. Adsorption equilibrium in zeolites	26
I.3.6.1. Unary adsorption equilibrium of gases and vapors on zeolites.....	26
I.3.6.2. Mixture adsorption equilibrium on zeolites: thermodynamic consistency.....	32
I.3.6.2. Adsorption measurement	33
I.3.7. Adsorption kinetics and diffusion in subnanoporous materials.....	34
I.3.7.1. Diffusivities in zeolites	34
I.3.7.2. Generalized Maxwell-Stefan diffusional theory: Maxwell-Stefan vs. Fickian (transport) diffusivities	35
I.3.7.3. Dependence of MS surface diffusivities with total loading.....	37
I.3.7.4. Equations for unary and multicomponent mass transfer within zeolites	38
I.4. ZEOLITE MEMBRANES: AN OVERVIEW.....	40
I.4.1. Preparation of zeolite membranes	40

I.4.1.1. Self-supported membranes.....	40
I.4.1.2. Composite or supported membranes.....	41
I.4.1.2.1. Dry gel method (DGM)	42
I.4.1.2.2. Liquid-phase hydrothermal synthesis	43
I.4.2. Microstructure of zeolite membranes: non-zeolite pores	53
I.4.3. Separations with zeolite membranes based on adsorption properties	55
I.4.3.1. Gas separation.....	55
I.4.3.2. Pervaporation of liquid mixtures.....	55
I.4.3.3. Zeolite membrane reactors.....	58
II. OBJECTIVES.....	61
III. EXPERIMENTAL SECTION.....	67
III.1. SYNTHESIS OF ZEOLITE NaA COMPOSITE MEMBRANES	69
III.1.1. Conditioning of the supports	70
III.1.2. Seeding techniques	71
III.1.2.1. Rubbing (brush-seeding)	71
III.1.2.2. Cross-flow filtration seeding.....	72
III.1.3. Preparation and characterization of synthesis gels	72
III.1.4. Hydrothermal syntheses	75
III.1.5. Synthesis of zeolite NaA membranes in a discontinuous glass vessel	76
III.1.6. Synthesis of zeolite NaA membranes in a semi-continuous synthesis system.....	78
III.1.6.1. Experimental set up.....	78
III.1.6.2. Experimental procedure	81
III.1.7. Synthesis of zeolite NaA membranes in a continuous synthesis system	83
III.1.7.1. Experimental set up.....	83
III.1.7.2. Experimental procedure	84
III.2. MEMBRANE CHARACTERIZATION TECHNIQUES.....	85
III.2.1. Characterization of <i>as</i> -synthesized zeolite NaA membranes.....	85
III.2.1.1. Permeation of pure gases at near ambient pressure	85
III.2.1.2. Vacuum pervaporation	86
III.2.1.3. Other analyses	89
III.2.2. Determination of PSDs in meso- and macroporous ceramic membranes in terms of flux measurements.....	70
III.2.2.1. Procedure I: pure Knudsen diffusion of a single gas.....	70

III.2.2.2. Procedure II: permeability of a pure liquid	92
III.2.2.3. Procedure III: non-hindered diffusion of an electrolyte	93
III.3. DETERMINATION OF EQUILIBRIUM AND KINETICS OF ADSORPTION..	96
III.3.1. Weight uptake in a microbalance (TGA).....	96
III.3.1.1. Experimental set up.....	96
III.3.1.2. Experimental procedure	98
III.3.2. Breakthrough curve analysis by mass spectrometry (MS)	99
III.3.2.1. Experimental set up.....	99
III.3.2.2. Experimental procedure	102
III.3.3. Adsorption isotherms of N ₂ at 77 K	105
III.4. SOLID CHARACTERIZATION TECHNIQUES.....	105
III.4.1. X-ray diffraction (XRD).....	105
III.4.2. Scanning electron microscopy (SEM) - Energy dispersive spectroscopy (EDS)	105
III.4.3. Transmission electron microscopy (TEM)	106
III.4.4. X-ray fluorescence (XRF)	106
III.4.5. Photon correlation spectroscopy (PCS).....	107
III.4.6. BET surface area and N ₂ adsorption isotherms at 77 K.....	107
III.4.7. Helium pycnometry	107
IV-VIII. RESULTS AND DISCUSSION.....	109
IV. PREPARATION AND CHARACTERIZATION OF OUTER- AND INNER-SIDE ZEOLITE NaA MEMBRANES ON TUBULAR CERAMIC SUPPORTS.....	109
IV.1. PRELIMINARY STUDIES.....	113
IV.1.1. Synthesis of zeolite NaA membranes and layers.....	113
IV.1.2. Rheological characterization of the synthesis gels.....	113
IV.2. CROSS-FLOW FILTRATION SEEDING: EFFECT OF THE OPERATING VARIABLES.....	116
IV.2.1. Effect of feed flow rate.....	116
IV.2.2. Effect of transmembrane pressure and crystal size	116
IV.2.3. Effect of pH.....	118
IV.3. PREPARATION OF OUTER- AND INNER-SIDE ZEOLITE NaA	

MEMBRANES.....	120
IV.3.1. Preparation of <i>outer-side</i> tubular zeolite NaA membranes in a discontinuous glass vessel with and without gel renewal.....	120
IV.3.2. Preparation of <i>inner-side</i> tubular zeolite NaA membranes in a discontinuous glass vessel with and without the presence of a centrifugal field.....	121
IV.3.2.1. Effect of the presence of a centrifugal field.....	122
IV.3.2.2. Effect of the concentration of the gel.....	124
IV.3.2.3. Effect of the seeding weight gain (SWG).....	126
IV.3.3. Preparation of inner-side tubular zeolite NaA membranes in a semi-continuous synthesis system.....	128
IV.3.3.1. Effect of the position of the membrane in the autoclave.....	129
IV.3.3.2. Effect of the gel renewal rate.....	133
IV.3.3.3. Effect of the seeding weight gain (SWG).....	133
IV.3.4. Preparation of inner-side tubular zeolite NaA membranes in a continuous synthesis system.....	137
IV.4. CHARACTERIZATION BY XRD AND SEM/EDS ANALYSES	138
IV.4.1. Characterization by XRD analyses.....	138
IV.4.2. Characterization by SEM/EDS analyses.....	142
IV.4.2.1. Seeded and unseeded supports.....	142
IV.4.2.2. Outer-side zeolite NaA membranes prepared in the semi-continuous system.....	143
IV.4.2.3. Inner-side zeolite NaA membranes prepared under a centrifugal field.....	144
IV.4.2.4. Inner-side zeolite NaA membranes prepared in the semi-continuous system.....	146
IV.4.2.5. Inner-side zeolite NaA membranes prepared in continuous system.....	146
IV.5. PV PERFORMANCE OF THE AS-SYNTHEZIZED MEMBRANES	151
IV.5.1. Summary of VPV results.....	151
IV.5.2. Effect of the N ₂ permeance and He/N ₂ ideal selectivity.....	154
IV.5.3. Effect of the weight gain after synthesis.....	158
IV.5.4. Effect of the SWG.....	158
IV.5.5. Effect of the number of synthesis cycles.....	162
IV.5.6. Stability of the membranes.....	164
IV.6. DISCUSSION AND FINAL REMARKS	165

V. PV DEHYDRATION OF ALCOHOL MIXTURES WITH ZEOLITE NaA MEMBRANES: APPLICATION TO ZEOLITE MEMBRANE REACTORS.....	169
V.1. GENERAL TRENDS FOR TOTAL FLUX AND SELECTIVITY TOWARDS DEHYDRATION OF ETHANOL/WATER MIXTURES BY VPV	171
V.1.1. Effect of the feed (retentate) pressure.....	171
V.1.2. Effect of the permeate pressure	172
V.1.3. Effect of the feed composition.....	173
V.1.4. Effect of the feed composition.....	176
V.1.5. Trend of permeate composition with feed composition ($Y_w - X_w$ curve).....	181
V.2. VPV PERFORMANCE TOWARDS THE DEHYDRATION OF BINARY AND TERNARY ORGANIC MIXTURES	182
V.2.1. Effect of the number of carbon atoms (C) of the alcohol	182
V.2.2. Effect of the feed composition.....	186
V.2.3. Effect of temperature	186
V.3. SIMULATION OF A MULTITUBULAR PV ZEOLITE NaA MEMBRANE REACTOR TO CARRY OUT THE LIQUID-PHASE ETHERIFICATION REACTION OF 1-PENTANOL TO DNPE	186
V.3.1. Stoichiometry and kinetics of the reaction	189
V.3.2. Modeling	190
V.3.2.1. Flow modeling in fixed-bed reactors.....	190
V.3.2.1.1. Velocity gradients normal to the flow direction due to wall effects.....	191
V.3.2.1.2. Axial dispersion.....	191
V.3.2.1.3. Velocity gradients caused by poor distribution of reactants	191
V.3.2.1.4. Radial temperature and concentration gradients.....	191
V.3.2.1.5. Channeling and shortcuts.....	192
V.3.2.2. External and internal mass transfer	192
V.3.2.3. Modeling of a zeolite NaA membrane reactor	192
V.3.3. Simulation results	193
V.4. DISCUSSION AND FINAL REMARKS	197
VI. CHARACTERIZATION OF POROUS MEMBRANES IN TERMS OF FLUX MEASUREMENT: APPLICATION TO CHARACTERIZATION OF LARGE DEFECTS IN ZEOLITE NaA MEMBRANES	199

VI.1. CHARACTERIZATION OF PSDs IN NF, UF AND MF MEMBRANES:	
MOMENT THEORY:	201
VI.1.1. Statistical moments of a pore size distribution.....	201
VI.1.1.1.0 th moment	202
VI.1.1.2. 1 st and 2 nd moments.....	202
VI.1.1.3. -k th moments ($k = 0 \rightarrow \infty$).....	204
VI.1.1.4. Structural parameters	206
VI.1.2. A special case: unimodal log-normal PSDs	206
VI.1.3. Characterization of PSDs in porous asymmetric membranes.....	208
VI.1.3.1. Contribution of the support.....	208
VI.1.3.2. Determination of experimental overall permeances.....	210
VI.1.3.2.1. Single-gas permeance experiments	210
VI.1.3.2.2. Pure liquid permeability experiments.....	212
VI.1.3.2.3. Non-hindered ionic diffusion experiments	214
VI.1.3.3. Membrane characterization in terms of $\bar{d}_{M,2}$ diameters and ϵ_S/τ_S	216
VI.2. CHARACTERIZATION OF INTERCRYSTALLINE LARGE DEFECTS	
IN ZEOLITE NaA MEMBRANES FROM VPV MEASUREMENTS	220
VI.2.1. Modeling.....	222
VI.2.1.1. Zone I: Liquid-filled volume in the capillary.....	224
VI.2.1.2. Zone II: Vapor-filled volume in the capillary	225
VI.2.1.3. Contribution of the macroporous support	225
VI.2.1.4. Equation for overall mass transfer	225
VI.2.2. Characterization of intercrystalline porosity in zeolite NaA membranes by	
VPV.....	227
VI.3. DISCUSSION AND FINAL REMARKS.....	233
VII. GAS AND VAPOR ADSORPTION EQUILIBRIUM ON ZEOLITES.....	235
VII.1. ADSORPTION EQUILIBRIUM OF WATER AND ETHANOL IN	
ZEOLITE NaA POWDER	237
VII.1.1. Characterization of the zeolite NaA (4A) commercial powder.....	237
VII.1.2. Unary adsorption isotherms of water and ethanol on zeolite NaA.....	240
VII.1.3. Prediction of binary adsorption isotherms of water and ethanol on zeolite	
NaA powder.....	249
VII.1.3.1. Ideal Adsorbed Solution Theory: preliminary simulations	249
VII.1.3.2. Binary adsorption isotherms of water and ethanol on zeolite NaA.....	250

VII.2. POTENTIAL THERMODYNAMIC ISOTHERM FOR MICROPOROUS MATERIALS (PTI). FORMULATION AND EXPERIMENTAL VALIDATION	258
VII.2.1. Potential thermodynamic isotherm (PTI).....	259
VII.2.2. Comparison between the PTI and the Dubinin-Astakhov isotherm.....	264
VII.2.3. Comparison between the PTI and the Langmuir isotherm.....	266
VII.2.4. Characterization of active carbons and zeolites by the PTI	270
VII.3. FINAL REMARKS	276
VIII. MODELING THE VPV PERFORMANCE IN ZEOLITE NaA MEMBRANES.....	279
VIII.1. DETERMINATION OF MS SURFACE DIFFUSIVITIES OF WATER AND ETHANOL VAPORS IN ZEOLITE NaA POWDER	281
VIII.1.1. External mass transfer (EMT)	282
VIII.1.2. Determination of MS surface diffusivities of water in zeolite NaA powder from weight uptake in a microbalance.....	283
VIII.1.3. Determination of MS surface diffusivities of water and ethanol from breakthrough curves obtained in a differential packed-bed.....	286
VIII.1.4. Fitting of experimental adsorption kinetic data of water and ethanol vapors to the model	287
VIII.1.5. Comparison with literature data.....	291
VIII.2. MODELING MASS TRANSFER ACROSS ZEOLITE NaA MEMBRANES IN THE VPV PROCESS	291
VIII.2.1. Mass transfer of adsorbed molecules by surface diffusion: Maxwell Stefan diffusional theory	294
VIII.2.2. Preliminary modeling: Extended Langmuir approach.....	295
VIII.2.2.1. Equations for water and surface fluxes	295
VIII.2.2.2. Weak confined MS surface diffusivities	297
VIII.2.2.3. Strong confined MS surface diffusivities	298
VIII.2.2.4. Fitting of experimental water and ethanol surface flux data	300
VIII.2.2.5. Correlations for surface fluxes and selectivities for membrane ZA2	300
VIII.2.2.6. Adsorption-diffusion vs. Solution-diffusion model.....	305
VIII.2.2.7. Discussion	305
VIII.2.3. PRAST approach + contribution of large defects.....	308
VIII.2.3.1. Modeling binary adsorption equilibria of water and ethanol.....	308
VIII.2.3.2. Equations for surface diffusion	309

VIII.2.3.3. Resolution of the model and fitting of experimental data	311
VIII.2.3.4. Correlations with experimental data.....	312
VIII.3. DISCUSSION AND FINAL REMARKS: ROLE OF GRAIN BOUNDARIES (NON-ZEOLITE PORES).....	316
IX. CONCLUSIONS AND FUTURE WORK	319
X. GLOSSARY	327
XI. REFERENCES.....	337
XII. APPENDICES	A.1
APPENDIX A : DETERMINATION OF MOLAR ADSORPTION LOADINGS FROM EXPERIMENTAL BREAKTHROUGH CURVES	A.3
APPENDIX B : PROGRAM TO SIMULATE A ZEOLITE MEMBRANE REACTOR.....	A.6
APPENDIX C : DETERMINATION OF ACTIVITY COEFFICIENTS OF A MIXTURE OF ADSORBED SPECIES.....	A.8
APPENDIX D : FITTINGS OF N₂ ADSORPTION ISOTHERMS AT 77 K TO THE TPI.....	A.11
APPENDIX E : ESTIMATION OF EXTERNAL MASS TRANSFER COEFFI- CIENTS (K_G)	A.21
APPENDIX F : PROGRAM FOR THE DETERMINATION OF MS SURFACE DIFFUSIVITIES FROM UNARY ADSORPTION KINETICS	A.24
APPENDIX G : PROGRAM FOR THE DETERMINATION OF ALPHA COEFFICIENTS IN EQS. VIII.66 AND VIII.67	A.31
XIII. ABSTRACT IN CATALAN LANGUAGE.....	B.1

