

# Contents

|   |           |
|---|-----------|
| <b>Acknowledgements / Agradecimientos (ES)</b>  | <b>1</b>  |
| <b>Abstract / Resumen (ES)/ Resumen (VAL)</b>   | <b>5</b>  |
| <b>List of symbols and abbreviations</b>  | <b>11</b> |
| <b>1 Introduction</b>   | <b>25</b> |
| 1.1 Zeolites . . . . .  | 26        |
| 1.1.1 A short history of zeolites . . . . .   | 26        |
| 1.1.2 Structure and composition . . . . .   | 28        |
| 1.1.3 Synthesis of zeolites . . . . .   | 34        |
| 1.1.4 Properties and applications . . . . .   | 38        |
| 1.2 Adsorption on nanoporous materials . . . . .                                      | 47        |
| 1.2.1 Basics of adsorption . . . . .  | 48        |
| 1.2.2 Swing adsorption processes . . . . .  | 54        |
| 1.3 Industrial separations . . . . .  | 57        |
| 1.3.1 Purification of hydrogen . . . . .  | 59        |
| 1.3.2 Separation of hydrogen isotopes . . . . .                                       | 62        |
| 1.3.3 Separation of carbon dioxide . . . . .  | 64        |
| 1.3.4 Separation of olefins from paraffins . . . . .                                  | 71        |
| 1.3.5 Separation of linear, branched and dibranched paraffins . . . . .               | 73        |
| 1.3.6 Separation of acetone, butanol and ethanol . . . . .                            | 74        |
| 1.3.7 Zeolites as adsorbents in other industrial and commercial separations . . . . . | 76        |

|   |            |
|---|------------|
| <b>2 Objectives</b>   | <b>81</b>  |
| <b>3 Materials and Methods</b>  | <b>83</b>  |
| 3.1 Characterization techniques and equipment . . . . .   | 83         |
| 3.1.1 X-Ray Diffraction . . . . .   | 83         |
| 3.1.2 Nuclear Magnetic Resonance . . . . .  | 83         |
| 3.1.3 Inductively Coupled Plasma Optical Emission Spectroscopy . . . . .                              | 87         |
| 3.1.4 Scanning electron microscopy . . . . .  | 87         |
| 3.1.5 Elemental Analysis . . . . .  | 87         |
| 3.1.6 Thermogravimetric analysis . . . . .  | 87         |
| 3.1.7 Adsorption for textural analysis . . . . .  | 88         |
| 3.2 Materials and their synthesis . . . . .   | 89         |
| 3.2.1 Nomenclature of zeolitic materials . . . . .  | 89         |
| 3.2.2 Synthesis of zeolitic materials . . . . .   | 91         |
| 3.2.3 Characterization results . . . . .  | 111        |
| 3.3 Adsorption experiments . . . . .  | 112        |
| 3.3.1 Gases and vapors used . . . . .   | 112        |
| 3.3.2 Adsorption isotherms of pure compounds . . . . .  | 112        |
| 3.3.3 Adsorption kinetics of pure compounds . . . . .   | 116        |
| 3.3.4 Dynamic mixture adsorption experiments . . . . .  | 117        |
| <b>4 Zeolite Si-RWR for the separation of light gases</b>   | <b>131</b> |
| 4.1 Characterization of Si-RWR samples . . . . .  | 133        |
| 4.2 Separation of hydrogen isotopes . . . . .   | 136        |
| 4.3 Separation of components present in steam methane reformer off gas and refinery off gas . . . . . | 140        |
| 4.3.1 Carbon dioxide from other SMROG components . .  | 140        |
| 4.3.2 Hydrogen from carbon monoxide . . . . .   | 148        |
| 4.4 Conclusions regarding the adsorption properties of zeolite Si-RWR . . . . .                       | 152        |
| <b>5 AlPOs and SAPOs as carbon dioxide adsorbents</b>   | <b>153</b> |
| 5.1 Characterization of the materials selected for this study . .                                     | 158        |

|          |  |            |
|----------|--|------------|
| 5.2      | Adsorption isotherms and isosteric heats of adsorption of carbon dioxide . . . . .   | 164        |
| 5.3      | Comparison of SAPOs, AlPOs and zeolites as adsorbents for the separation of CO <sub>2</sub> from CH <sub>4</sub> . . . . .     | 170        |
| 5.4      | Conclusions regarding AlPOs and SAPOs as carbon dioxide adsorbents . . . . .   | 173        |
| <b>6</b> | <b>Influence of zeolite framework topology on the separation of carbon dioxide from methane</b>                                | <b>175</b> |
| 6.1      | Materials description and characterization . . . . .   | 178        |
| 6.2      | Pure component isotherms analysis . . . . .  | 180        |
| 6.3      | Breakthrough adsorption experiments . . . . .  | 186        |
| 6.4      | Conclusions on the influence of zeolite framework topology on the separation of CO <sub>2</sub> from CH <sub>4</sub> . . . . . | 200        |
| <b>7</b> | <b>Zeolite Si-STW for the separation of linear, branched and dibranched paraffins</b>  | <b>201</b> |
| 7.1      | Materials description and characterization . . . . .   | 202        |
| 7.2      | Selection of model adsorbates and methodology . . . . .  | 203        |
| 7.3      | Comparison between Si-STW and Si-MFI materials as adsorbents for the separation of pentane isomers . . . . .                   | 206        |
| 7.3.1    | Adsorption isotherms and selectivities of C5 isomers on Si-STW and Si-MFI materials . . . . .                                  | 206        |
| 7.3.2    | Isosteric heats of adsorption of C5 isomers on Si-MFI and Si-STW and comparison with literature data                           | 209        |
| 7.3.3    | Kinetics of adsorption of C5 isomers on Si-STW and Si-MFI materials . . . . .  | 210        |
| 7.4      | Si-STW as an adsorbent for the separation of hexane and heptane isomers . . . . .  | 214        |
| 7.4.1    | Adsorption isotherms and selectivities of C6 and C7 isomers on Si-STW . . . . .  | 214        |
| 7.4.2    | Isosteric heats of adsorption of C6 and C7 isomers on Si-STW . . . . .   | 217        |

|  |            |
|--|------------|
| 7.4.3 Kinetics of adsorption of C6 and C7 isomers on Si-STW . . . . .  | 218        |
| 7.5 Conclusions on the use of zeolite Si-STW for the separation of linear, branched and dibranched paraffins . . . . . | 222        |
| <b>8 Vapor phase separation of acetone, butanol and ethanol using Si-STT</b>   | <b>223</b> |
| 8.1 Materials description and characterization . . . . .   | 224        |
| 8.2 Pure component vapor isotherms . . . . .   | 227        |
| 8.3 Breakthrough adsorption experiments . . . . .  | 230        |
| 8.3.1 Basic experiments analysis . . . . .   | 230        |
| 8.3.2 Experiments carried out at different conditions . . . . .  | 234        |
| 8.3.3 Desorption data analysis . . . . .   | 236        |
| 8.4 Comparison of Si-STT with Si-LTA as adsorbents for the ABE separation from the vapor phase . . . . .               | 240        |
| 8.5 Conclusions on the vapor phase ABE separation on Si-STT  | 244        |
| <b>9 Other work related to this thesis</b>   | <b>245</b> |
| 9.1 Adsorption properties of ITQ-69 . . . . .  | 245        |
| 9.2 Roads to nowhere . . . . .   | 245        |
| 9.2.1 Quasi-elastic Neutron Scattering for the study of propane and propene diffusion in zeolite Si-LTA . . . . .      | 245        |
| 9.2.2 Development of the VOLGRAV method . . . . .  | 246        |
| <b>10 Conclusions</b>  | <b>249</b> |
| <b>A Appendix to chapter 6</b>   | <b>251</b> |
| A.1 XRD patterns and $^{29}\text{Si}$ MAS NMR spectra . . . . .  | 251        |
| A.2 Estimation of isotherms at 25 °C on Si-ITW . . . . .   | 255        |
| A.3 Breakthrough and regeneration profiles . . . . .   | 257        |
| <b>B Appendix to chapter 7</b>   | <b>267</b> |
| B.1 XRD patterns and $^{29}\text{Si}$ MAS NMR spectra . . . . .  | 267        |

|   |            |
|---|------------|
| <b>C Appendix to chapter 8</b>                                  | <b>270</b> |
| C.1 XRD patterns and $^{29}\text{Si}$ MAS NMR spectra . . . . . | 270        |
| <b>Bibliography</b>   | <b>273</b> |