

**Index**

Chapter 1: Introduction.....	1
1.1 Zeolites .....	1
1.1.1 Zeolites structure and classification.....	1
1.1.1.1 Zeolite structure .....	2
1.1.1.2 Zeolites chemical composition.....	4
1.1.1.3 Classification of zeolites .....	4
1.1.2 Properties of zeolites .....	5
1.1.2.1 Adsorption capacity of zeolites.....	5
1.1.2.2 Ionic exchange in zeolites .....	6
1.1.2.3 Acid and basic properties of zeolites .....	6
1.1.3 Applications of zeolites .....	7
1.1.3.1 Catalysis.....	7
1.1.3.2 Adsorption and separation .....	8
1.1.3.3 Ionic exchange .....	8
1.1.3.4 Environmental applications.....	8
1.1.3.5 Other applications .....	9
1.2 Synthesis of zeolites .....	9
1.2.1 Synthesis mechanism of zeolites .....	10
1.2.2 Parameters in the synthesis of zeolites .....	12
1.2.3 Hydrothermal synthesis of zeolites.....	14
1.2.4 Ionothermal synthesis of zeolites .....	15
1.2.5 Dry gel synthesis of zeolites .....	15
1.2.6 Post-synthesis treatments of zeolites .....	16
1.2.6.1 Dealumination of zeolites .....	16
1.2.6.2 Desilication of zeolites.....	17
1.2.6.3 Phosphorus incorporation in zeolites .....	17
1.3 Structure Directing Agents (SDA's) of zeolites .....	18
1.3.1 Inorganic SDA's .....	19
1.3.2 Organic SDA's .....	20
1.3.2.1 Alkylammonium cations as OSDA's .....	21
1.3.2.2 Phosphorous cations as OSDA's.....	22
1.3.2.3 Sulfonium cations as OSDA's .....	32
1.3.2.4 Arsonium cations as OSDA's .....	32
1.3.2.5 Oxo crown macrocycles (crown ethers) OSDA's .....	32
1.3.2.6 Metal complexes and organometallic OSDA's .....	32

1.3.2.7 Self-assembled OSDA's .....	33
1.3.2.8 Ionic liquids OSDA's .....	34
1.3.2.9 Deep eutectic solvents (DES) OSDA's .....	35
1.4 References.....	36
Chapter 2: Objectives.....	67
Chapter 3: Experimental section .....	69
3.1 Characterization techniques .....	69
3.1.1 X-Ray Diffraction .....	69
3.1.1.1 Phase identification .....	70
3.1.1.2 Structural elucidation.....	70
3.1.2 Chemical analyses.....	71
3.1.3 Thermogravimetric analyses .....	72
3.1.4 Textural properties .....	72
3.1.4.1 Surface area and micropore volume determination .....	73
3.1.4.2 Micropore size distribution determination.....	75
3.1.5 Nuclear magnetic resonance .....	75
3.1.5.1 Phosphorus NMR .....	78
3.1.5.2 Silicon NMR.....	78
3.1.5.3 Fluorine NMR .....	79
3.1.5.4 Aluminium NMR .....	79
3.1.5.5 NMR spectrometers and data collection.....	80
3.1.6 Acidity of zeolites .....	81
3.1.6.1 Fourier Transform-Infrared spectroscopy using pyridine as probe molecule	81
3.1.6.2 Ammonia Thermoprogrammed Desorption (TPD) .....	83
3.1.7 Electron microscopy techniques .....	83
3.1.7.1 Scanning Electron Microscopy (SEM).....	84
3.1.7.2 Energy Dispersive X-Ray spectroscopy (EDX) .....	84
3.1.7.3 Transmission Electron Microscopy (TEM) .....	85
3.1.7.4 Electron Diffraction Tomography (EDT).....	85
3.2 Methods and materials .....	86
3.2.1 OSDA synthesis .....	86
3.2.1.1 OSDA-1: tetraethylammonium cation (TEA) .....	87
3.2.1.2 OSDA-2: tetraethylphosphonium cation (TEP).....	88
3.2.1.3 OSDA-3: methyl-tris-(dimethylamino)-phosphonium cation (MNP) .....	89
3.2.1.4 OSDA-4: methyl-tri-isopropylphosphonium cation (MIP) .....	91
3.2.1.5 OSDA-5: di-isopropyl-diethylammonium cation (IEN).....	93

## *Synthesis and characterization of zeolitic materials using P-OSDA*

---

3.2.1.6 OSDA-6: phosphazene base P1-t-Bu (PB1) .....	95
3.2.1.7 OSDA-7: tris(diethylamino)(methyl)phosphonium cation .....	96
3.2.1.8 OSDA-8: butane - 1,4-diylbis [tris(dimethylamino) phosphonium] cation (PN-PN) .....	98
3.2.1.9 OSDA-9: butane-1,4-diylbis(triisopropylphosphonium) cation .....	100
3.2.1.10 OSDA-10: tris(dimethylamino) [4-(tri-tert-butylphosphonio) butyl] phosphonium cation .....	102
3.2.1.11 OSDA-11: Butane-1,4-diylbis(triethylphosphonium) cation .....	105
3.2.2 Synthesis gel preparation .....	107
3.2.2.1 OSDA stability studies .....	109
3.2.2.2 Dual template synthesis of MFI (ZSM-5, TS-1) zeolite .....	111
3.2.2.3 Dual template synthesis of RTH (RUB-13) zeolite .....	113
3.2.2.4 Synthesis of IWV (ITQ-27) zeolite .....	114
3.2.2.5 Synthesis of DON (UTD-1) zeolite .....	116
3.2.2.6 Synthesis of ITQ-58 zeolite .....	117
3.2.2.7 Synthesis of ITQ-66 zeolite .....	119
3.2.3 Removal of OSDA 's .....	120
3.2.3.1 Calcination under air .....	121
3.2.3.2 High temperature treatment under H <sub>2</sub> stream .....	122
3.2.3.3 Washing of residual phosphorous species .....	124
3.3 References .....	125
Chapter 4: Study on Stability of OSDA 's .....	129
4.1 Introduction .....	129
4.2 Experiment 1: effect of the hydrothermal parameters on OSDA 's in MFI synthesis .....	132
4.2.1 Solid products .....	132
4.2.1.1 Crystallinity of solid products .....	133
4.2.1.2 Chemical analyses of solid products .....	135
4.2.2 Mother liquor analyses .....	138
4.2.2.1 Quantification .....	138
4.2.2.2 OSDA stability .....	139
4.3 Experiment 2: generalized study of the OSDA stability .....	144
4.3.1 Solid products .....	144
4.3.1.1 Crystallinity of solid products .....	145
4.3.1.2 Chemical analyses of solid products .....	148
4.3.2 Mother liquor analyses .....	149
4.3.2.1 OSDA stability .....	149

4.4	Conclusions.....	153
4.5	References.....	154
Chapter 5: Phosphorus Modified Zeolites.....		155
5.1	Introduction.....	155
5.2	MFI zeolite.....	156
5.2.1	Dual template P-modified all-silica MFI zeolite .....	157
5.2.1.1	Chemical analyses of as-made P-modified all-silica MFI zeolite.....	160
5.2.1.2	Morphology of as-made P-modified all-silica MFI zeolite .....	162
5.2.1.3	Thermogravimetric analysis of as-made P-modified all-silica MFI zeolite.....	163
5.2.2	Dual template P-modified aluminosilicate MFI zeolite .....	164
5.2.2.1	Chemical analyses of as-made P-modified aluminosilicate MFI zeolite.....	165
5.2.2.2	Morphology of P-modified aluminosilicate MFI zeolite .....	168
5.2.2.3	Thermogravimetric analysis of as-made P-modified aluminosilicate MFI zeolite .....	169
5.2.3	Thermal treatments of P-modified aluminosilicate MFI zeolite .....	170
5.2.3.1	Crystallinity of thermally treated P-modified aluminosilicate MFI zeolite .....	171
5.2.3.2	Chemical analyses of thermally treated P-modified aluminosilicate MFI zeolite .....	172
5.2.3.3	Textural properties of P-modified MFI zeolite.....	173
5.2.3.4	Acidic properties of thermally treated aluminosilicate MFI zeolite .....	174
5.2.4	NMR analyses of P-modified aluminosilicate MFI zeolite.....	176
5.2.4.1	OSDA incorporation and species .....	176
5.2.4.2	Aluminium incorporation and species .....	180
5.3	RTH zeolite.....	184
5.3.1	Dual template synthesis of RTH zeolite.....	185
5.3.1.1	Synthesis conditions .....	185
5.3.1.2	Phase crystallinity.....	186
5.3.2	Sample analyses of as-made P-modified RTH zeolite .....	187
5.3.2.1	Chemical analyses of as-made P-modified RTH zeolite .....	187
5.3.2.2	Morphology of as-made P-modified RTH zeolite .....	189
5.3.2.3	Thermogravimetric analysis of as-made P-modified RTH zeolite .....	190
5.3.3	Thermal treatments of P-modified RTH zeolite.....	192
5.3.3.1	Crystallinity of thermally treated P-modified RTH zeolite .....	192
5.3.3.2	Chemical analyses of thermally treated P-modified RTH zeolite.....	193
5.3.3.3	Textural properties of thermally treated P-modified RTH zeolite.....	193
5.3.3.4	Acidic properties of thermally treated RTH zeolite.....	195
5.3.4	NMR study of P-modified RTH zeolite .....	196

5.3.4.1	OSDA incorporation and species .....	196
5.3.4.2	Aluminium incorporation and species .....	200
5.4	NMR study of phosphorus species in P-modified MFI and RTH .....	205
5.4.1	Proton-phosphorus interaction.....	205
5.4.2	Aluminium-phosphorus interaction.....	207
5.5	Conclusions .....	210
5.6	References .....	212
Chapter 6:	Synthesis of ITQ-27 (IWV) and UTD-1 (DON) Zeolites .....	219
6.1	Introduction .....	219
6.2	Synthesis .....	220
6.2.1.1	Synthesis conditions.....	220
6.2.1.2	Phase crystallinity .....	222
6.3	ITQ-27 (IWV) zeolite.....	225
6.3.1	Sample analyses of as-made IWV zeolite.....	226
6.3.1.1	Chemical analyses of as-made IWV zeolite.....	226
6.3.1.2	Morphology of as-made IWV zeolite .....	227
6.3.1.3	Thermogravimetric analysis of the as-made IWV zeolite.....	228
6.3.2	Thermal treatments of IWV zeolite .....	229
6.3.2.1	Crystallinity of thermally treated IWV zeolite.....	230
6.3.2.2	Chemical analyses of thermally treated IWV zeolite .....	231
6.3.2.3	Morphology of thermally treated IWV zeolite.....	232
6.3.2.4	Textural properties of thermally treated IWV zeolite .....	233
6.3.2.5	Acidic properties of thermally treated IWV zeolite .....	235
6.3.3	NMR study of the IWV zeolite.....	237
6.3.3.1	Incorporation and stability of the OSDA into the IWV zeolite.....	237
6.3.3.2	Aluminium incorporation in the IWV zeolite .....	240
6.3.3.3	Boron incorporation in the IWV zeolite.....	244
6.3.3.4	Fluorine incorporation in the IWV zeolite framework.....	244
6.3.3.5	Silicon framework of the IWV zeolite .....	246
6.4	UTD-1 (DON) zeolite .....	250
6.4.1	Sample analyses of as-made DON zeolite.....	251
6.4.1.1	Chemical analyses of as-made DON zeolite .....	252
6.4.1.2	Morphology of as-made DON zeolite.....	252
6.4.1.3	Thermogravimetric analysis of the as-made DON zeolite .....	254
6.4.2	Thermal treatments on the DON zeolite.....	255
6.4.2.1	Crystallinity of thermally treated DON zeolite .....	256

6.4.2.2	Chemical analyses of thermally treated DON zeolite.....	257
6.4.2.3	Morphology of thermally treated DON zeolite.....	258
6.4.2.4	Textural properties of thermally treated DON zeolite .....	259
6.4.3	NMR study of the DON zeolite .....	260
6.4.3.1	Incorporation and stability of the OSDA to the DON zeolite.....	260
6.4.3.2	Aluminium incorporation in the DON zeolite .....	263
6.5	Conclusions.....	265
6.6	References.....	266
Chapter 7:	Synthesis of New Zeolite Materials .....	271
7.1	Introduction.....	271
7.2	ITQ-58 zeolite.....	272
7.2.1	Previous work: aminophosphonium OSDA .....	272
7.2.1.1	Synthesis conditions .....	273
7.2.1.2	PN-PN ITQ-58 chemical analyses.....	274
7.2.1.3	Morphology of PN-PN ITQ-58 zeolite.....	275
7.2.1.4	Thermogravimetric analysis of the PN-PN ITQ-58 zeolite .....	276
7.2.1.5	Structural resolution attempts .....	276
7.2.2	Phosphonium cation OSDA .....	277
7.2.2.1	Synthesis.....	277
7.2.2.2	PC-PC ITQ-58 chemical analyses .....	279
7.2.3	Phosphonium-aminophosphonium OSDA .....	281
7.2.3.1	Synthesis.....	281
7.2.3.2	PN-PC ITQ-58 chemical analyses .....	283
7.2.3.3	Morphology of PN-PC ITQ-58 zeolite .....	284
7.2.3.4	Thermogravimetric analysis of the PN-PC ITQ-58 zeolite .....	284
7.2.3.5	NMR analyses of the ITQ-58 zeolite.....	286
7.2.4	Textural properties of the ITQ-58 zeolite .....	290
7.2.5	Structural resolution of the ITQ-58 zeolite .....	291
7.2.5.1	Unit cell parameters.....	292
7.2.5.2	ITQ-58 zeolite building .....	293
7.3	ITQ-66 zeolite.....	295
7.3.1	Synthesis .....	295
7.3.1.1	Synthesis conditions .....	296
7.3.1.2	Phase crystallinity.....	297
7.3.2	Sample analyses of the ITQ-66 zeolite .....	297
7.3.2.1	Chemical analyses of the ITQ-66 zeolite.....	298

7.3.2.2	Morphology of the ITQ-66 zeolite.....	298
7.3.2.3	Thermogravimetric analysis of the as-made ITQ-66 zeolite.....	299
7.3.3	Thermal treatments of the ITQ-66 zeolite .....	300
7.3.3.1	Crystallinity of thermally treated ITQ-66 zeolite.....	301
7.3.3.2	Chemical analyses of thermally treated ITQ-66 zeolite.....	302
7.3.3.3	Morphology of thermally treated ITQ-66 zeolite.....	303
7.3.3.4	Textural properties of the ITQ-66 zeolite .....	304
7.3.4	Structural resolution of the ITQ-66 zeolite.....	306
7.3.4.1	Description of the unit cell of the ITQ-66.....	306
7.3.4.2	Channel system description of the ITQ-66 .....	308
7.3.4.3	Location of heteroatoms in ITQ-66.....	308
7.3.5	NMR analyses of the ITQ-66 zeolite.....	309
7.3.5.1	Incorporation and stability of the OSDA into the ITQ-66 zeolite.....	310
7.3.5.2	Gallium incorporation into the ITQ-66 zeolite .....	313
7.3.5.3	Boron incorporation into the ITQ-66 zeolite.....	314
7.3.5.4	Fluorine incorporation into the ITQ-66 zeolite framework.....	315
7.3.5.5	Silicon framework of the ITQ-66 zeolite .....	316
7.4	Conclusions .....	318
7.5	References .....	319
Chapter 8:	Conclusions.....	325
8.1	General conclusions .....	325
8.2	OSDA stability .....	326
8.3	Phosphorous-modified zeolite .....	326
8.4	Synthesis of IWV and DON zeolites.....	328
8.5	Synthesis of new zeolite materials .....	329