Synthesis and Characterisation of Nanoporous and Core-Shell Zeotype Materials

Alexis Oliver Schmidt

UCL

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy (Chemistry)

Declaration

I, Alexis Oliver Schmidt, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Abstract

The main objective of the PhD thesis project is to explore the synthetic aspects and gel chemistry of small pore zeolitic materials, both silicoaluminophosphate and aluminosilicate zeolites. Herein, variations of SAPO-34 and shell@core type synthesis methods involving SAPO-34, SSZ-13, and silicalite-1 were studied. Correlations between structural properties and stability of shell@core type nanoporous systems were established via laboratory-based characterisation techniques, with X-ray diffraction (XRD) being the primary analysis tool.

First, SAPO-34 synthesis methods and its gel chemistry were investigated to improve directed incorporation of silicon into the zeolite framework and enhance its stability. Following calcination runs on processing-dependent as-synthesised SAPO-34 samples derived from precipitated SiO₂ with 10 mol% Si in the reactant gel via a successive order of addition, it was discovered these experienced the least deterioration on their CHA framework.

Next, shell@core synthesis variations for silicalite-1@SAPO-34 compositions were explored to understand the gel chemistry behind these structure formations and increase in their stability. The aim was to modify the surface structure of SAPO-34 by growing a continuous hydrophobic silicalite-1 shell over SAPO-34 core crystals that can shield the core from water and maintain its desired stability. Because the CHA framework topology in specific products appears undamaged after condensation of TEOS with acetic acid, it appears to be that amorphous SiO₂ has accumulated on the surface of SAPO-34 crystals and preserved these in the very alkaline synthesis medium of the reactant gel.

Finally, shell@core synthesis alternatives for compositions with SSZ-13, an aluminosilicate which is isostructural to SAPO-34, were studied to unravel their gel chemistry. In the case of silicalite-1@SSZ-13 materials, the CHA phase of SSZ-13 appears to be slowly superseded by the MFI phase of silicalite-1 with protracted crystallization times. This may point to recrystallization of the CHA framework topology of SSZ-13 to the MFI type of ZSM-5.

3

Impact Statement

Apart from delivering outstanding results as a methanol-to-olefin (MTO) catalyst, SAPO-34 (CHA zeolite) is a prime candidate for application in the selective catalytic reduction (SCR) of NO_x under an oxidizing atmosphere in the exhaust gas of diesel or lean-burn engines, and as such has been garnering the attention of research groups worldwide. Silicoaluminophosphates (SAPOs), which can be produced via the isomorphous substitution of P in the microporous AIPO₄ or AI/P islands by Si, possess the cation-exchange properties found in CHA (aluminosilicate) zeolites and can form the same small-pore crystalline structure. Results from literature and patents indicate that Cu ion-exchanged SAPO-34 presents high activity towards NO_x reduction with NH₃ or C₃H₆. Currently, the main concern of study is its thermal stability combined with detailed characterisation and how the crystallinity and structural properties are affected over extended periods of time. To tackle these issues, modification of the surface structure of SAPOs has been proposed through the growth of a continuous shell with a distinct zeotype framework over SAPO core crystals (shell@core materials) while still maintaining the desired catalytic properties.

The research project has a potentially far-reaching impact as the goal is to propel the development of novel catalytic materials with less expensive and non-toxic compounds such as silica, alumina, phosphates and copper for production of vehicle emission control catalysts. Various types of precious metal containing catalysts exist around the world which can efficiently reduce the emission of toxic gases from vehicles. Nevertheless, there is a strong incentive to find alternative solutions involving less expensive metals which exhibit a similar or superior performance. Domestic, commercial and industrial consumers, policy makers, regulators as well as specific research communities would benefit from the results of this study. When confronted with the reality of rising demand in an expanding global economy, such initiatives are necessary to fulfil agreed emission control targets. Given the opportunity to develop the technology into a mature product with reasonable costs, it can be adopted and manufactured by business to then be launched in the market.

4

Table of Contents

Declara	ation.	
Abstrac		
Impact	State	ement4
Table o	of Co	ntents5
List of F	-igur	es9
List of 7	Fable	es17
Acknow	vledg	pements20
Chapte	r 1: I	ntroduction21
1.1	Bac	kground21
1.2	Stru	uctural Chemistry of Zeolites21
1.2	.1	Building Units of Zeolites
1.2	.2	Zeolite Pore Sizes
1.2	.3	Brønsted-Acid Sites27
1.2.4 Hydro(solvo)therma		Hydro(solvo)thermal Synthesis
1.3	SAF	PO Materials34
1.3	.1	SAPO-3435
1.3	.2	SAPO-18
1.3	.3	SAPO-56
1.3	.4	SAPO-35
1.4	Alte	ernative Zeotype Materials40
1.5	Cor	e-shell and Hybrid SAPOs/Zeolites41
1.5	.1	Overview41
1.5	.2	ZSM-5/SAPO-34 Composite
1.5	.3	ZSM-5/SAPO-11 Composite
1.5	.4	ZSM-5/SAPO-5 Composite43
1.5	.5	Beta/SAPO-11 Composite44

1.6 Syste	Synthesis ems	of	ZSM-5/SAPO-34	and	SAPO-34/ZSM-5	Composite
1.6	5.1 Synthe	esis P	rocedure Scheme			45
1.6	5.2 Synthe	esis Pa	arameters and XR	D Patt	ern Results	48
1.7	Standard N	NH₃ So	elective Catalytic F	Reduct	ion	50
1.7	7.1 Overvi	iew				50
1.7	′.2 NH₃-S	CR M	echanisms			52
1.7	.3 Hydrot	therma	al Stability during I	NH₃-S(CR of NO _x	55
1.8	Alcohol-to-	-Olefir	s Processes			58
1.9	Project Air	ns and	d Objectives			59
Chapte	er 2: Experin	nental	Techniques and N	/lethoc	lologies	62
2.1	Chapter O	vervie	w			62
2.2	Hydrotherr	mal Sy	nthesis Technique	э		62
2.3	Powder X-	Ray D	Diffraction			63
2.4	Electron M	licroso	copy Techniques			66
2.4	.1 Scann	ing El	ectron Microscopy	·		66
2.4	.2 Energ	y-Disp	ersive X-ray Spec	trosco	ру	68
2.5	X-ray Phot	toelec	tron Spectroscopy			68
2.6	Ultraviolet-	Visibl	e Spectroscopy			70
2.7	Infrared Sp	oectro	scopy			70
2.8	Solid-state	Nucle	ear Magnetic Reso	onance	Spectroscopy	72
Chapte	er 3: Impact	of SA	PO-34 Synthesis	Paran	neters on Structura	l Properties,
and Co	mparison w	ith Sm	nall/Medium Pore 2	Zeolite	S	74
3.1	Chapter O	vervie	w			74
3.2	Introductio	n				74
3.3	Experimen	ntal				77
3.3	8.1 Synthe	esis				77
3.3	3.2 Chara	cterisa	ation			83

3.4 Results and Discussion85
3.4.1 Powder X-ray Diffraction85
3.4.2 Scanning Electron Microscopy and Energy-Dispersive X-ray
Spectroscopy104
3.4.3 Solid-state Nuclear Magnetic Resonance Spectroscopy108
3.4.4 Infrared Spectroscopy114
3.5 Conclusions and Discussion116
Chapter 4: Investigation of Synthesis Methods for Silicalite-1@SAPO-34 Structures and Contrast with Analogous Zeolite Blends
4.1 Chapter Overview
4.2 Introduction
4.3 Experimental
4.3.1 Synthesis120
4.3.2 Characterisation
4.4 Results and Discussion131
4.4.1 Powder X-ray Diffraction131
4.4.2 Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy158
4.4.3 X-ray Photoelectron Spectroscopy164
4.4.4 Ultraviolet-Visible Spectroscopy168
4.5 Conclusions and Discussion169
Chapter 5: Investigation of Synthesis Methods for Shell@Core Structures with
SSZ-13, and Contrast with Analogous Zeolite Blends
5.1 Chapter Overview
5.2 Introduction
5.3 Experimental177
5.3.1 Synthesis177
5.3.2 Characterisation

5.4	Re	sults and Discussion	.183
5.4	l.1	Powder X-ray Diffraction	.183
5.4	1.2	Scanning Electron Microscopy	.193
5.4	1.3	X-ray Photoelectron Spectroscopy	.194
5.4	l.4	Solid-state Nuclear Magnetic Resonance Spectroscopy	.196
5.4	1.5	Infrared Spectroscopy	.198
5.5	Со	nclusions and Discussion	.199
Chapte	er 6:	Conclusions and Future Work	.202
6.1	Co	nclusions	.202
6.2	Fut	ture Work	.206
Refere	nces	S	.208
Append	dices	5	.219
7.1	Pa	wley Refinement of Powder X-Ray Diffraction Patterns	.219
7.2	Ele	emental Mapping with Energy-Dispersive X-ray Spectroscopy	.222
7.3	Ele	ement Scan Ranges in X-ray Photoelectron Spectroscopy	.224

List of Figures

Figure 1.1: (a) TO_4 tetrahedron; (b) TO_4 tetrahedra linked through a common
oxygen vertex ² 22
Figure 1.2: Secondary building units and their respective codes ¹⁰ 24
Figure 1.3: Depiction of typical zeolite pore sizes with oxygen-packing
<i>models</i> ^{15,16} 27
Figure 1.4: Chemical structure of a Brønsted-acid site ¹⁷ 28
Figure 1.5: Cell parameters, composite building units and CHA-framework of
SAPO-34 with a hexagonal lattice system ¹² 36
Figure 1.6: Cell parameters, composite building unit and AEI-framework of
SAPO-18 with an orthorhombic lattice system ⁴⁹
Figure 1.7: Cell parameters, composite building units and AFX-framework of
SAPO-56 with a hexagonal lattice system ⁵⁸
Figure 1.8: Cell parameters, composite building units and LEV-framework of
SAPO-35 with a hexagonal lattice system ⁶⁴
Figure 1.9: Schemes of ZSM-5/SAPO-34 (top) and SAPO-34/ZSM-5 (bottom)
composite overall synthesis procedure ⁷² 47
Figure 1.10: XRD diffractograms of SAPO-34/ZSM-5 and ZSM-5/SAPO-34
composite molecular sieves, as well as SAPO-34 and ZSM-5 standards: (a)
SAPO-34, (b) SZ1, (c) SZ2, (d) ZS1, (e) ZS2 and (f) ZSM-5 ⁷² 49
Figure 1.11: Adapted portrayal of the catalytic cycle for standard SCR reaction
over metal-exchanged zeolite catalysts. Acid sites correspond to Lewis or
Brønsted sites at ion-exchanged metal or free proton sites. Redox sites are
represented by isolated or binuclear oxo-metal ion-exchanged sites ^{1,113} 53
Figure 1.12: Adapted SCR cycle proposal over Cu-SSZ-13 (isostructural to Cu-
SAPO-34) at 473 K. Oxidized Cu (top) and its reduced (bottom) halves of the
redox cycle are divided by the dotted line ^{1,114} 54
Figure 1.13: Adapted mechanism proposal for SCR of NO with NH3 over Cu-
SSZ-13 comprising an NO ⁺ intermediate ^{1,117} 55
Figure 2.1: Setup of autoclave for the hydrothermal method ¹⁵⁰ 63
Figure 2.2: Depiction of fundamental principles of x-ray diffraction ¹⁵⁴ 65
Figure 2.3: Portrayal of measurement principle of SEM ¹⁶⁰ 67

Figure 2.4: Schematic depiction of a standard XPS setup, including examples of XP spectra from four different metals as a function of core level photoemission intensity against the binding energy with element specific distribution¹⁶².......69 Figure 2.5: FTIR absorbance spectra of H/SAPO-34 and Cu/SAPO-34 samples after thermal treatment at 500°C¹⁶⁴.....72 Figure 3.1: Illustration of the structure of the CHA framework¹²......76 Figure 3.2: XRD patterns of CHA standard and three processing-dependent assynthesised SAPO-34 samples derived from Ludox® AS-40 colloidal SiO₂. Figure 3.3: XRD patterns of CHA standard and three processing-dependent assynthesised SAPO-34 samples derived from precipitated SiO₂. Normalized Figure 3.4: XRD patterns of CHA standard and three processing-dependent assynthesised SAPO-34 samples derived from tetraethyl orthosilicate. Normalized Figure 3.5: XRD patterns of CHA standard and three processing-dependent assynthesised SAPO-34 samples derived from microspherical SiO₂. Normalized intensity is plotted against the diffraction angle 2 θ90 Figure 3.6: XRD patterns of a CHA standard and six processing-dependent assynthesised SAPO-34 samples derived from microspherical SiO₂ with 10 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ......93 Figure 3.7: XRD patterns of a CHA standard and six processing-dependent assynthesised SAPO-34 samples derived from microspherical SiO₂ with 25 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ......94 Figure 3.8: XRD patterns of a CHA standard and six processing-dependent assynthesised SAPO-34 samples derived from precipitated SiO₂ with 10 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ . Figure 3.9: XRD patterns of a CHA standard and six processing-dependent assynthesised SAPO-34 samples derived from precipitated SiO₂ with 25 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 3.10: XRD patterns of a CHA standard and five calcined SAPO-34 samples derived from microspherical SiO₂ with 10 mol% Si in reaction gel. Figure 3.11: XRD patterns of a CHA standard and five calcined SAPO-34 samples derived from precipitated SiO₂ with 10 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ100 Figure 3.12: XRD patterns of LEV, AFV, CHA, and MFI standards, and samples targeting SAPO-57 (10 mol% Si), ZnAPO-57, CoAPO-34 and silicalite-1. Normalized intensity is plotted against the diffraction angle 2 θ102 Figure 3.13: XRD patterns of AFV and LEV standards and two as-synthesised SAPO-57 samples derived from microspherical SiO₂ with 25 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ103 Figure 3.14: SEM images of 110116[A]_{...}_spc (10 mol% Si, microspherical SiO₂ as Si precursor, order of addition 1) [a,b,c] and 120116[A] {...}_spc (10 mol% Si, microspherical SiO₂ as Si precursor, order of addition 2) [d,e,f].105 Figure 3.15: EDS spectra coupled with SEM images of SAPO-34 samples 190116[A] {...} spc/c900 [a,b] and 190116[A] {...} lpc/c900 [c,d] (both ^{1}H MAS NMR of SAPO-34 Figure 3.16: spectra samples 190116[A]_{...}_spc/c900 [top] and 190116[A]_{...}_lpc/c900 [bottom] (both Figure 3.17: 27AI MAS NMR spectra of SAPO-34 samples 190116[A] {...} spc/c900 [top] and 190116[A] {...} lpc/c900 [bottom] (both Figure 3.18: ²⁹Si MAS NMR spectra with deconvolution results of SAPO-34 samples 190116[A] {...} spc/c900 [top] and 190116[A] {...} lpc/c900 [bottom] (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor)......112 31**P** Figure 3.19: MAS NMR spectra of SAPO-34 samples 190116[A]_{...}_spc/c900 [top] and 190116[A]_{...}_lpc/c900 [bottom] (both Figure 3.20: Transmittance FTIR spectra of commercial SAPO-34 at different temperatures......115

Figure 3.21: Transmittance ATR-FTIR spectra of SAPO-34 samples 190116[A]_{...}_spc/c900 [blue] and 190116[A]_{...}_lpc/c900 [red] (both Figure 4.1: XRD patterns of CHA and MFI standards and three attempted assynthesised silicalite-1@CoAPO-34 materials. Normalized intensity is plotted Figure 4.2: XRD patterns of CHA and MFI standards and four attempted assynthesised silicalite-1@SAPO-34 materials. Normalized intensity is plotted Figure 4.3: XRD patterns of CHA and MFI standards, commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials (without ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction Figure 4.4: XRD patterns of CHA and MFI standards, commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials prior to calcination (with ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against Figure 4.5: XRD patterns of CHA and MFI standards, commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials after calcination (with ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the Figure 4.6: XRD patterns of MFI standard, dry silicalite-1 gel and three silicalite-1 samples with different crystallization times. Normalized intensity is plotted against the diffraction angle 2 θ144 Figure 4.7: XRD patterns of CHA and MFI standards and four samples targeting silicalite-1@SAPO-34 materials (without ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction angle 2 θ145 Figure 4.8: XRD patterns of CHA and MFI standards, double ion exchanged commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials following 3 h, 5 h, 7 h and 9 h crystallization (with ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction

Figure 4.9: XRD patterns of CHA and MFI standards, double ion exchanged commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34

1 with reduced pH value in reactant gel. Normalized intensity is plotted against the diffraction angle 2 θ154

Figure 4.15: XRD patterns of MFI standard, condensed SiO₂, and three samples targeting silicalite-1 without iPrOH in reactant gel following 24 h, 48 h and 144 h crystallization. Normalized intensity is plotted against the diffraction Figure 4.16: SEM images of commercial SAPO-34 [a,b], and of attempted silicalite-1@SAPO-34 190117[A]_{...}_s@c,sol/c550 samples (3 h crystallization) [c], 190117[B]_{...}s@c,sol/c550 (5 h crystallization) [d], (7 h 190117[C]_{...}_s@c,sol/c550 crystallization) and [e] 190117[D]_{...}s@c,sol/c550 (9 h crystallization) [f] (ion-exchanged SAPO-34 seed crystals)......160

Figure 4.17: SEM images of silicalite-1 (24 h crystallization) [a] and of attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-34(24h/AcOH) [b], Silicalite-

Figure 5.3: XRD patterns of CHA and MFI standards, previously as-synthesised SSZ-13 sample with and without condensed SiO₂, and three samples targeting silicalite-1@SSZ-13 materials after hydrolysis condensation following 24 h, 48 h and 144 h crystallization. Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 5.4: XRD patterns of CHA and MFI standards, commercial SSZ-13, and four samples targeting recrystallization of SSZ-13 to ZSM-5 with and without

hydrolysis condensation following 24 h, 48 h and 144 h crystallization. Figure 5.5: SEM images of as-synthesised SSZ-13(24h-age/144h) [a,b] and of commercial SSZ-13 [c,d]......194 Figure 5.6: Atomic percentage of the XPS assessed elements (Si, O) for assynthesised SSZ-13(24h-age/144h), commercial SSZ-13 and as-synthesised Figure 5.7: ¹H MAS NMR spectrum of commercial SSZ-13......197 Figure 5.8: ²⁷AI MAS NMR spectrum of commercial SSZ-13......197 Figure 5.9: ²⁹Si MAS NMR spectrum with deconvolution results of commercial Figure 5.10: Transmittance FTIR spectra of commercial SSZ-13 at different temperatures......199 Figure 7.1: Pawley refinement of XRD pattern of the processing-dependent assynthesised SAPO-34 sample 190116[A]_{...}_spc (derived from precipitated SiO₂ with 10 mol% Si in reaction gel, order of addition 1)......219 Figure 7.2: Pawley refinement of XRD pattern of the processing-dependent assynthesised SAPO-34 sample 190116[A]_{...}_lpc (derived from precipitated SiO₂ with 10 mol% Si in reaction gel, order of addition 1)......219 Figure 7.3: Pawley refinement of XRD pattern of the processing-dependent assynthesised SAPO-34 sample 190116[B]_{...}_fc (derived from precipitated SiO₂ with 10 mol% Si in reaction gel, order of addition 1)......220 Figure 7.4: Pawley refinement of XRD pattern of silicalite-1@SAPO-34 sample following 24 h crystallization (with hydrolysis condensation of TEOS with AcOH Figure 7.5: Pawley refinement of XRD pattern of silicalite-1@SAPO-34 sample following 48 h crystallization (with hydrolysis condensation of TEOS with AcOH Figure 7.6: Pawley refinement of XRD pattern of silicalite-1@SAPO-34 sample following 144 h crystallization (with hydrolysis condensation of TEOS with AcOH Figure 7.7: Pawley refinement of XRD pattern of silicalite-1@SSZ-13 sample following 24 h crystallization (with hydrolysis condensation of TEOS with AcOH

Figure 7.8: Pawley refinement of XRD pattern of silicalite-1@SSZ-13 sample following 48 h crystallization (with hydrolysis condensation of TEOS with AcOH Figure 7.9: Pawley refinement of XRD pattern of silicalite-1@SSZ-13 sample following 144 h crystallization (with hydrolysis condensation of TEOS with AcOH Figure 7.10: EDS spectrum coupled with SEM image of Cu(II) ion-exchanged commercial SAPO-34 [a,g], including elemental mapping of Si [b], AI [c], P [d], Figure 7.11: Survey XPS spectrum [a] of commercial SAPO-34, including highlighted element scan ranges of Si [b], AI [c], P [d] and O [e].225 Figure 7.12: Survey XPS spectrum [a] of silicalite-1@SAPO-34 sample following 144 h crystallization (with hydrolysis condensation of TEOS with AcOH as an intermediary step and without iPrOH in reactant gel), including highlighted element scan ranges of Si [b], AI [c], P [d] and O [e]......226 Figure 7.13: Survey XPS spectrum [a] of commercial SSZ-13, including highlighted element scan ranges of Si [b] and O [c]......227

List of Tables

Table 1.1: List of SBUs present in zeolite structures ² . 26
Table 1.2: Commonly utilized solvents in solvothermal synthesis and their
respective parameter values (units are excluded) ²³ 32
Table 1.3: Common zeolite structures and their respective SDAs ²⁵ .
Table 1.4: Synthesis parameters of ZSM-5/SAPO-34 and SAPO-34/ZSM-5
composite molecular sieves ⁷² 49
Table 3.1: Orders of addition, crystallization method and product recovery steps
for hydrothermal synthesis of SAPO-3480
Table 3.2: Order of addition, crystallization method and product recovery steps
for hydrothermal synthesis of SAPO-5781
Table 3.3: Used Si-precursor, goodness of fit, cell parameters and crystallite
size of processing-dependent as-synthesised SAPO-34 samples calculated
using Pawley refinement86
Table 3.4: Used Si-precursor, -content, order of addition, goodness of fit, cell
parameters and crystallite size of processing-dependent as-synthesised SAPO-
34 samples calculated using Pawley refinement92
34 samples calculated using Pawley refinement92 Table 3.5: Used Si-precursor, -content, order of addition, goodness of fit, cell
34 samples calculated using Pawley refinement92 Table 3.5: Used Si-precursor, -content, order of addition, goodness of fit, cell parameters and crystallite size of calcined SAPO-34 samples calculated using
34 samples calculated using Pawley refinement
34 samples calculated using Pawley refinement. 92 Table 3.5: Used Si-precursor, -content, order of addition, goodness of fit, cell parameters and crystallite size of calcined SAPO-34 samples calculated using Pawley refinement. 98 Table 3.6: Targeted and actual zeotype phase & class, goodness of fit, cell parameters and crystallite size of SAPO-57, ZnAPO-57, CoAPO-34 and silicalite-1 calculated using Pawley refinement. 101 Table 4.1: Performed synthesis plan of shell@core materials of silicalite-1 1@CoAPO-34 and silicalite-1@SAPO-34 as a function of seed crystal mass per silicalite-1 gel volume. 121 Table 4.2: Performed synthesis plan of silicalite-1@SAPO-34 materials as a function of crystallization time and pre-treatment of SAPO-34 core via ion exchange. 123
34 samples calculated using Pawley refinement

exchange; double ion exchanged SAPO-34, dry silicalite-1 gel and silicalite-1 are also listed......125 Table 4.4: Mechanical mixtures of commercial SAPO-34 with as-synthesised Table 4.5: Performed synthesis plan of silicalite-1 and silicalite-1@SAPO-34 Table 4.6: Sample list for Cu(II) ion exchange involving commercial SAPO-34 and three samples targeting silicalite-1@SAPO-34 materials derived from hydrolysis condensation following 24 h, 48 h and 144 h crystallization......129 Table 4.7: Targeted and actual zeotype phase, class, seed crystal mass per gel volume, goodness of fit, cell parameters and crystallite size of shell@core Table 4.8: Targeted and actual zeotype phase, class, goodness of fit, cell parameters and crystallite size of commercial SAPO-34 and attempted silicalite-Table 4.9: Targeted and actual zeotype phase, class and crystallization time of double ion exchanged commercial SAPO-34, dry silicalite-1 gel, silicalite-1 and attempted silicalite-1@SAPO-34 materials......143 Table 4.10: Targeted and actual zeotype phase, goodness of fit, cell parameters and crystallite size of mechanical mixtures of SAPO-34 with silicalite-1 calculated using Pawley refinement......149 Table 4.11: Targeted and actual zeotype phase, goodness of fit, cell parameters and crystallite size of silicalite-1 and silicalite-1@SAPO-34 materials calculated using Pawley refinement......151 Table 5.1: Performed synthesis plan of SSZ-13 and SSZ-13@SAPO-34 materials as a function of crystallization time......178 Table 5.2: Mechanical mixtures of as-synthesised SSZ-13 with commercial SAPO-34 according to employed weight ratios......179 Table 5.3: Performed synthesis plan of silicalite-1@SSZ-13 materials as a Table 5.4: Performed recrystallization plan of SSZ-13 to ZSM-5 as a function of synthesis medium and crystallization time......181

 Table 5.5: Targeted and actual zeotype phase, goodness of fit, cell parameters

 and crystallite size of mechanical mixtures of SSZ-13 with SAPO-34 calculated

 using Pawley refinement.
 184

 Table 5.6: Targeted and actual zeotype phase, goodness of fit, cell parameters

 and crystallite size of SSZ-13 and SSZ-13@SAPO-34 materials calculated

 using Pawley refinement.

 185

 Table 5.7: Targeted and actual zeotype phase, goodness of fit, cell parameters

 and crystallite size of SSZ-13 and SSZ-13@SAPO-34 materials calculated

 using Pawley refinement.

 185

 Table 5.7: Targeted and actual zeotype phase, goodness of fit, cell parameters

 and crystallite size of SSZ-13 with and without condensed SiO₂, and silicalite

 1@SSZ-13 materials calculated using Pawley refinement.

 188

 Table 5.8: Targeted and actual zeotype phase, goodness of fit, cell parameters

 and crystallite size of SSZ-13 with and without condensed SiO₂, and silicalite

 1@SSZ-13 materials calculated using Pawley refinement.

 188

 Table 5.8: Targeted and actual zeotype phase, goodness of fit, cell parameters

 and crystallite size of SSZ-13 and its recrystallization products calculated using

 Pawley refinement.
 191

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Chapter 1: Introduction

1.1 Background

A noteworthy drop in emissions of hydrocarbons, CO and NO_x from gasoline powered vehicles has been achieved thanks to the introduction of the three-way catalyst as the active component of the catalytic converter, a common component present on vehicles in Europe and in the US for more than 30 years¹. However, it should be pointed out that three-way catalytic converter technology is not apt for use on lean-burn engines, such as diesel-powered vehicle engines, which function under high air/fuel ratios¹. The inability of the three-way catalyst to diminish NO_x emissions at elevated air/fuel ratios is what hinders the widespread adoption of these lean-burn engine technologies, despite them being in principle more fuel efficient than "stoichiometric" gasoline power-trains¹. To address the issues behind lean-NO_x emission control, significant studies have been taken via the commercialization of two novel nano-materials-based catalytic emission control applications for diesel-powered vehicles. These are the NO_x storage/reduction (NSR) catalyst and the selective catalytic reduction with ammonia (NH₃-SCR) incorporating metal-exchanged zeolites¹. Nonetheless, key issues such as performance, stability and costs must be overcome before the effective application of these technologies. Microporous zeolitic materials have been found to be very good candidates to act as catalysts for, in particular, NH₃-SCR reactions.

1.2 Structural Chemistry of Zeolites

Amongst microporous materials, zeolites are considered the most important family of systems with ordered pores. From a historical point of view, the term 'zeolite' stands for a silica polymorph or crystalline aluminosilicate comprised of corner-sharing TO_4 (T = Si or Al) tetrahedral which constitute a three-dimensional four-connected framework with uniformly sized pores of molecular dimensions. Today, the term 'zeolite framework' generally is generally associated with a corner sharing network of tetrahedrally coordinated atoms². However, it should be pointed out that the framework elements are not confined to just AI and Si atoms, and that other primary building units apart from tetrahedra are also possible. In fact, most of the elements in the periodic table have been incorporated as framework atoms in microporous materials³.

1.2.1 Building Units of Zeolites

The primary building units of zeolites, namely TO₄ tetrahedra, contain framework T atoms which are commonly represented by Si, Al or P atoms. [SiO₄], [AlO₄], or [PO₄] tetrahedra are thus the standard structural building units of the zeolite framework. Other elements, for instance Be, B, Ga, Ge, etc., may also adopt the role of framework T atom². As can be observed in Figure 1.1, each T atom is tetrahedrally surrounded by four oxygen atoms [example (a)], which in turn act as bridges between T atoms [example (b)]. For this reason, the structure type of a zeolite features a (4;2)-connected framework. However, there are cases of zeolites which possess five- or six-coordinated Al atoms with one or two extra-framework oxygen species (OH or H₂O), in conjunction with four-coordinated Al atoms².



Figure 1.1: (a) TO₄ tetrahedron; (b) TO₄ tetrahedra linked through a common oxygen vertex².

As a result of aluminosilicate zeolites being assembled from SiO₄ tetrahedra and AlO₄ tetrahedra, the framework is anionic. This leads to the negative charge being compensated by extra-framework cations. Given this fact, the empirical formula of an aluminosilicate zeolite can be represented as $A_{x/n}[Si_{1-x}Al_xO_2] \cdot m H_2O$, with A symbolizing a metal cation of valence n^2 .

Adsorbed water molecules and cations can be found in the channels or cages of this kind of zeolites. In the case of aluminophosphate molecular sieves consisting of strictly alternating AlO₄ and PO₄ tetrahedra via corner sharing, they exhibit a neutral framework⁴. For this reason, there are no extra metal cations in the framework, but instead adsorbed water molecules or templating molecules which have settled in the channels.

According to Löwenstein's Rule, structures of aluminosilicate zeolites do not form AI-O-AI linkages⁵. Likewise, aluminophosphate-based molecular sieves tend to not display certain linkages, such as P-O-P, P-O-Si, AI-O-AI, Me-O-AI, and Me-O-Me (where M stands for metal)⁶.

The framework of a zeolite can be regarded as being composed of finite component units or infinite component unit-like chains and layers². Meier^{7,8} and Smith⁹ proposed the idea behind infinite component units, which includes secondary building units (SBUs). There are 18 kinds of SBUs that can be found in tetrahedral frameworks¹⁰. These are portrayed in Figure 1.2. The illustrated SBUs can hold up to 16 tetrahedrally coordinated atoms (T-atoms) and are derived under the assumption that the entire framework consists of a limited number of SBU, with cases featuring one type of SBU only². Furthermore, it should be pointed out that SBUs are always nonchiral and that a unit cell invariably possesses an integral number of these units¹¹.



Figure 1.2: Secondary building units and their respective codes¹⁰.

Table 1.1 sums up the SBUs of numerous structure types of zeolites which are listed in the database of zeolite structures¹². As can be inferred from the table, several SBUs can constitute one type of framework. For instance, the CHA framework, which encompasses related materials such as chabazite, SAPO-34 and AIPO-34, comprises four kinds of SBUs. These are 4, 6, 6-6 and 4-2 units and can be used to depict the CHA framework². There are cases of frameworks that cannot be formed by just a single type of SBU, in other words combinations of SBUs are required. LOV, MEP and other clathrasil-type frameworks are just a few of various examples that exhibit this characteristic. Nonetheless, it should be pointed out that SBUs are just theoretical topological building units. They should not be contemplated as species which may be present in the solution or gel during the crystallization phase of a zeolitic compound².

Zeolite frameworks feature distinctive cage-building units, which are generally defined according to the *n*-rings that outline their faces. For instance, a truncated octahedron or sodalite unit that possesses six 4-rings and eight 6rings on its surface can be called a $[4^{6}6^{8}]$ cage. This nomenclature for sections of cages was established by Smith⁹. Should a polyhedral pore have at least one face outlined by a large enough ring through which a guest species can pass through, yet is not infinitely extended like a channel, then it should be named a cavity following IUPAC recommendations¹³.

With exceptions, SAPO frameworks can be generated in multiple ways via isomorphic substitutions of P and AI atoms in AIPO₄-based frameworks with Si. On the whole, isomorphic substitution mechanisms (SMs) are divided into three main categories: i) SM I (not applicable to Si) - substitution of AI atoms, which is further subdivided to SM I*a*, SM I*b* and SM I*c* and correspond respectively to monovalent, divalent and trivalent element substitution of AI atoms, leading to an M-O-P bond; ii) SM II - substitution of P atoms, which is subdivided to SM II*b* and symbolize respectively tetravalent and pentavalent element substitutions, thus resulting in an M-O-AI bond; iii) SM III – substitution of pairs of adjacent AI and P atoms, with Si, Ti and other tetravalent elements exhibiting this behaviour².

Most reports of SAPO materials indicate a combination of SM II*a* and SM III as the underlying mechanisms behind the incorporation of Si. Various synthetic parameters can influence substitution, for instance the Si content, the kind of organic template, the pH value, the amine/Al₂O₃ and P₂O₅/Al₂O₃ ratios in the reaction mixture, the temperature and the crystallization time². As a general rule, mechanism SM II*a* delineates how the first Si atom is assimilated into the framework. Once a critical Si concentration is surpassed, which can be substantially lower than the stoichiometric SM II*a* substitution level, SM III starts to play an active role as well, resulting in extensive regions in the individual crystals that become siliceous. It can also occur that Si atoms in silicon patches are replaced with AI atoms, giving rise to negative framework charges².

Code	SBU	Code	SBU	Code	SBU
ABW	4, 8	ERI	4, 6	OSI	6-2
ACO	4, 4-4, 8	ESV	5-1	OSO	combination
AEI	4, 6, 4-2, 6-6	ETR	4	OWE	4, 4-4-
AEL	10, 4-1	EUO	1-5-1	-PAR	4
AEN	4, 6	FAU	4, 6, 6-6, 6-2, 4-2, 1-4-1	PAU	4, 8
AET	6	FER	5-1	PHI	4, 8
AFG	4, 6	FRA	6, 4	PON	4-2
AFI	4, 6, 12	GIS	4, 8	RHO	4, 6, 8, 8-8
AFN	4, 8	GIU	4, 6	-RON	combination
AFO	4-1, 2-6-2	GME	4, 6, 8, 12, 4-2, 6-6	RRO	4-4=1
AFR	4, 6-2, 4-4	GON	5-3	RSN	combination
AFS	6*1	GOO	-4-4-	RTE	6, 5-1
AFT	4, 6, 6-6, 4-2	HEU	4-4=1	RTH	4
AFX	4, 6, 6-6, 4-2	IFR	6-2	RUT	6
AFY	4, 4-4	IHW	combination	RWR	6-2
AHT	4-2, 6	ISV	6-2	RWY	8, 3*1
ANA	4, 6, 6-2, 4-[1,1], 1-4-1	ITE	4	SAO	4
APC	4, 8	ITH	combination	SAS	4, 6-2
APD	4, 8, 6-2	ITW	1-4-1, 4-[1,1]	SAT	6, 4
AST	4-1	IWR	1-5-1	SAV	4, 6, 4-2, 6-6
ASV	4-1	IWW	1-5-1	SBE	4, 8
ATN	4, 8	JBW	6	SBS	4, 8
ATO	4, 6, 12	KFI	4,6, 8, 6-6, 6-2, 4-2	SBT	4
ATS	4, 6, 12	LAU	6, 1-4-1	SFE	combination
ATT	4-2, 6	LEV	6	SFF	5-3
ATV	4-[1,1], 6	LIO	6, 4	SFG	combination
AWO	6, 4-2, 4	-LIT	6, 4-[1,1], 4-2	SFH	5-3
AWW	4, 6	LOS	4, 6, 6-2	SEN	5-3
BCT	4, 8	LOV	combination	SFO	6-2, 4-4-, 4
*BEA	combination	LTA	4, 6, 8, 1-4-1, 4-4, 6-2	SGT	5-3
BEC	6-2	LTL	6, 4-2	SOD	6
BIK	5-1	LTN	6, 4-2	SOS	4-2
BOG	4, 6, 5-1	MAR	6, 4	SSY	combination
BPH	6*1	MAZ	4-2, 5-1	STF	5-3
BRE	4	MEI	combination	STI	4-4=1
CAN	4, 6, 12	MEL	5-1	STT	5-3
CAS	5-1	MEP	combination	TER	2-6-2, 4-1
CDO	5-1	MER	4, 8, 8-8	THO	4=1
CFI	5-[1,1,1]	MEL	5-1	TON	5-1
CGF	4-1-1	MFS	combination	TSC	4, 6, 8, 4-2,
					6-6, 8-8
CGS	4	MON	4	UEI	4, 6, 4-2
CHA	4, 6, 6-6, 4-2	MOR	5-1	UFI	8
-CHI	5-[1,1]	MOZ	combination	UOZ	4-1
-CLO	4, 4-4	MSO	2-6-2, 4-1	USI	4-1
CON	5-2	MTF	5-5=1	UTL	combination
CZP	4, 4-[1,1]	MTN	combination	VET	combination
DAC	5-1	MTT	5-1	VFI	18, 6, 4-2
DDR	combination	MTW	5-[1,1]	VNI	combination
DFO	combination	MWW	combination	VSV	combination
DFT	4	NAB	4-1, 1-3-1	WEI	spiro-5
DOH	combination	NAT	4=1	-WEN	combination
DON	5-3	NES	combination	YUG	4, 8
EAB	4, 6	NON	combination	ZON	4, 6-2, 4-4-
EDI	4=1	NPO	3		
EMT	4,6, 6-6, 6-2, 4-2, 1-4-1	NSI	5-1		
EON	5-1	OBW	combination		
EPI	5-1	OFF	6, 4-2		

Table 1.1: List of SBUs present in zeolite structures².

1.2.2 Zeolite Pore Sizes

Zeolites present pore sizes which range from 0.3 to 1.0 nm, as well as pore volumes which go from 0.10 to $0.35 \text{ cm}^3/\text{g}^{14}$. For a better understanding, typical zeolite pore sizes are illustrated with oxygen-packing models^{15,16}. These

can be observed in Figure 1.3. Small pore zeolites, for example zeolite A, exhibit eight-ring pores with free diameters of 0.30 to 0.45 nm. As for medium zeolites, such as ZSM-5, these possess ten-ring pores that spans from 0.45 to 0.60 nm in free diameter¹⁴. In addition, large pore zeolites, which include zeolites X and Y, feature 12-ring pores of 0.6 to 0.8 nm. Lastly, there are also extra-large pore zeolites that contain 14-ring-pores and have dimensions of 0.7 to 1.0 nm, e.g. UTD-1¹⁴. Nevertheless, it should be pointed out that the zeolite framework is moderately flexible, since the size and shape of the framework and pore are susceptible to variations in temperature and different kinds of guest species.



Figure 1.3: Depiction of typical zeolite pore sizes with oxygen-packing models^{15,16}.

1.2.3 Brønsted-Acid Sites

Zeolites exhibit both Lewis and Brønsted acidity, with Brønsted-acid sites being constituted by bridging hydroxyl groups that behave as proton donors (Figure 1.4). On the other hand, the chemical nature of Lewis-acid sites is still a matter of research and debate. Octahedrally or tetrahedrally coordinated extraframework aluminum (EFAL) species, as well as tri-coordinated framework aluminum have been denoted as Lewis acid sites¹⁷. Furthermore, [AIO]⁺ species removed from the framework have been inferred as "true" Lewis-acid sites from X-ray diffractometry investigations¹⁸. Besides these assertions, experimental evidence suggests that Brønsted-acid sites are mainly responsible for catalytic activity¹⁹.



Figure 1.4: Chemical structure of a Brønsted-acid site¹⁷.

Four methods, which involve post-synthesis modifications, can be utilized for forming Brønsted-acid sites on zeolites. One option is presented in Equation 1.1, where a mineral acid is employed for the direct ion exchange of, for instance, zeolite Y via substitution of Na⁺. The cation is present due to its use as a SDA (structure directing agent) for the synthesis of the zeolite framework. A great disadvantage of this method is its aggressiveness, since a strong mineral acid would provoke dealumination. The zeolite framework would consequently decompose and collapse, particularly in those cases where the n_{Si} / n_{Ai} ratio is low²⁰.

$$H^+ + Na^+Y^- \xrightarrow{-Na^+} H^+Y^-$$
(1.1)

An alternative option for generating Brønsted-acid sites is via ion exchange with NH_4^+ -salts in aqueous solution and successive thermal decomposition of the NH_4^+ -ions. This is depicted in Equation 1.2. The main advantage of this method is the correlation between the amounts of NH_4^+ -salt added for the ion exchange and the resulting ratios of Brønsted-acid sites. Therefore, one can regulate the extent of the ion exchange.

$$NH_4^+ + Na^+Y^- \longrightarrow NH_4^+Y^- \xrightarrow{300 - 400 \circ C} H^+Y^-$$
 (1.2)

The third possibility, as is represented by Equation 1.3, consists of performing an ion exchange with multivalent cations, such as La³⁺ or Mg²⁺, and then proceeding with a thermal dehydration of the cationic complex²¹. In this case, the so-called Hirschler-Plank mechanism is involved in the formation of Brønsted-acid sites²². By thermally removing most of the water molecules in the cationic complex, the remaining water molecules begin to dissociate into hydroxide anions and protons due to the effect of strong electrostatic fields within the zeolite pores. Because of this phenomenon, the hydroxide anions are bound to the extra-framework multivalent cation. On the other hand, protons coordinate to oxygen atoms that are bound to aluminum in the zeolite framework. With a trivalent cation like La³⁺, it is possible to attain up to two Brønsted-acid sites.

$$[La(H_{2}O)_{n}]^{3+} + 3 Na^{+}Y^{-} \xrightarrow{-3 Na^{+}} [La(H_{2}O)_{n}]^{3+}(Y^{-})_{3}$$

$$\xrightarrow{300 \ ^{\circ}C} [La(OH)(H_{2}O)]^{2+}H^{+}(Y^{-})_{3} \longrightarrow [La(OH)_{2}]^{+}(H^{+})_{2}(Y^{-})_{3}$$
(1.3)

As can be gathered from Equation 1.4, the fourth alternative implies the use of a noble metal salt in an ion exchange. This is followed by thermal dissociation of the noble metal complex. By introducing molecular hydrogen, the noble metal ion is then reduced and a Brønsted-acid site is generated. The final Brønsted acidity can therefore be regulated via the initial charge of the noble metal salt, although the amount of acid sites tends to be relatively low²¹.

$$[Pt(NH_{3})_{4}]^{2+} + 2 Na^{+}Y^{-} \xrightarrow{-2 Na^{+}} [Pt(NH_{3})_{4}]^{2+}(Y^{-})_{2}$$

$$\xrightarrow{300 \ ^{\circ}C} Pt^{2+}(Y^{-})_{2} \xrightarrow{+H_{2}} Pt^{0}(H^{+})_{2}(Y^{-})_{2} \qquad (1.4)$$

1.2.4 Hydro(solvo)thermal Synthesis

Hydro(solvo)thermal synthesis involves synthetic reactions carried out within the temperature range from 100 to 1000 °C and a pressure range from 1 to 100 MPa in aqueous or organic solvents inside a specially sealed container or high-pressure autoclave under subcritical or supercritical conditions²³. Hydrothermal syntheses routes and related hydrothermal reactions have gained considerable relevance for the preparation of most inorganic functional materials, for instance microporous and porous materials, inorganic compounds with special compositions, structures, and condensed states and special morphology such as nano and ultra-fine powders, sol-gels, noncrystalline states, inorganic membranes, and single crystals²³.

In contrast to normal conditions, the properties of water experience a dramatic change under high temperature and pressure hydrothermal conditions. Parameters such as vapor pressure and ion product increase, whereas density, surface tension and viscosity diminish. Due to the elevated pressure and temperature hydrothermal conditions, the reaction rate is accelerated amongst the complex ions, the hydrolysation reaction is boosted, and the redox potential of the reactants is significantly altered²³. There are generally two kinds of basic chemical reactions. One the one hand is the ionic reaction, which encompasses the metathetical reaction of inorganic salts that could be instantly carried out at room temperature. On the other hand there is the free radical reaction, which comprises explosive reactions of organic compounds. It should be noted that other chemical reaction may share some of the aforementioned reaction characteristics. In consonance with the electron theory, reactions of organic compounds bearing polar bonds tend to exhibit similarities with ionic reactions²³. For this reason, if the medium is aqueous and the temperature of the system is brought above water's boiling point in a sealed container, an

30

increase of the ionic reaction rate will most certainly take place. Consequently, the high temperature and pressure (hydrothermal) conditions can positively induce the ionic or hydrolysis reaction for organic compounds or minerals which are insoluble at room temperature thanks to the higher ionization constant of water stemming from elevated temperatures²³.

In the case of solvothermal synthesis, it can be performed in numerous organic solvents with distinct properties that contribute to the formation of new structures. To this day, several alcohols have been employed for solvothermal synthesis²³. When using an alcohol as solvent, it is important to bear in mind what function it will assume during synthesis. This is because the solvent, apart from providing a medium, also wholly or partially dissolves the reactants. A solvent-reactant complex is then generated which will determine the chemical reaction rate. Because the solvent influences the concentration and state of the active species of the reactants, it is possible to modify the reaction process. For this purpose, organic solvents are generally classified on the basis of macroscopic and microscopic molecular parameters and empirical solvent polar parameters of compounds. These include molecular weight (M_r) , density (d), melting point (mp), boiling point (bp), molecular volume, heat of evaporation, dielectric constant (ϵ), dipole moment (μ), and solvent polarity (E_N^T). When defining the solvation properties of a solvent, the solvent polarity is the parameter of choice²³. It encompasses the sum of the interactions of solvent and solute, which includes the Coulombic, dispersion, charge-transport and induction forces, as well as the H-bond. A series of solvents typically used for solvothermal synthesis and their respective parameter values can be gathered from Table 1.2. Since only hydrothermal synthesis of zeolites is performed in the research project, only the properties of water as a solvent are relevant.

Solvent	M _r	d	mp	bp	3	μ	E_N^T
Tetradecanol	214.39	0.823	39	289			
2-Methyl-2-hexanol	116.20	0.8119		139.4			
2-Methyl-2-butanol	88.15	0.805	-12	102	7.0	1.70	0.321
2-Methyl-2-propanol	74.12	0.786	25	83			0.389
2-Pentanol	88.15	0.809		120	13.8	1.66	
Cyclohexanol	100.16	0.963	21	160	15.0	1.90	0.500
2-Butanol	74.12	0.807	-115	98	15.8		0.506
2-Propanol	60.10	0.785	-90	82	18.3	1.66	0.546
1-Heptanol	116.20	0.822	-36	176	12.1		0.549
2-Methyl-1-propanol	74.12	0.802	-10	108	17.7	1.64	0.552
1-Hexanol	102.18	0.814	-52	157	13.3		0.559
3-Methyl-1-butanol	88.15	0.809	-11	130	14.7	1.82	0.565
1-Pentanol	88.15	0.811	-78	137	13.9	1.80	0.568
1-Butanol	74.12	0.810	-90	118	17.1	1.66	0.602
Benzyl alcohol	108.14	1.045	-15	205	13.1	1.70	0.608
1-Propanol	60.10	0.804	-127	97	20.1	1.66	0.602
Ethanol	46.07	0.785	-130	78	24.3	1.69	0.654
Tetraethylene glycol	194.23	1.125	-6	314			0.664
1,3-Butanediol	90.12	1.004	-50	207			0.682
Triethylene glycol	150.18	1.123	-7	287	23.7	5.58	0.704
1,4-Butanediol	90.12	1.017	16	230	31.1	2.40	0.704
Diethylene glycol	106.12	1.118	-10	245			0.713
1,2-Propanediol	76.10	1.036	-60	187	32.0	2.25	0.722
1,3-Propanediol	76.10	1.053	-27	214	35.0	2.50	0.747
Methanol	32.04	0.791	-98	65	32.6	1.70	0.762
3,3'-Oxybis-1,2-propanedic	ol 166.18	1.300					
Ethylene glycol	62.07	1.109	-11	199	37.7	2.28	0.790
Glycerol	92.09	1.261	20	180	42.5		0.812
Water	18.01	1.000	0	100	80.4	1.94	1.000

Table 1.2: Commonly utilized solvents in solvothermal synthesis and their respective parameter values (units are excluded)²³.

A considerable amount of zeolites and microporous materials are most effectively synthesised via the hydrothermal synthetic-approach. Under hydrothermal synthetic conditions, the effective solvation ability of water is improved, the solubility of the reactants rises, and the reactivity of the source materials enhances. This enables the rearrangement and dissolution of the primary gel generated in the first stage of synthesis, thus increasing the nucleation and crystallization rate. As a general rule, the hydrothermal synthesis process is divided into two stages, these being the initial formation of the hydrated aluminosilicate gel and the subsequent crystallization of the gel. It should be noted that the mechanism governing the crystallization process is complicated and has not yet been completely elucidated²³. Independently of any suggested liquid- or solid-phase transformation mechanism, it is common convention that four steps constitute the crystallization process, namely: (1) condensation of polysilicate and aluminate anions; (2) nucleation of zeolites; (3) growth of nuclei; and lastly (4) crystal growth of zeolites that can eventually unfold itself to secondary nucleation²³. Understanding the formation mechanism and crystallization process of zeolites remains an issue due to: a) the whole crystallization process involving complicated chemical reactions; b) the nucleation and growth of crystals being carried out under heterogeneous conditions; and c) the process fluctuating continuously. Furthermore, there is also the setback of not having practical in situ measurement tools to establish the structure of the gel and solution²³.

Templates or SDAs which are typically utilized in the synthesis of inorganic microporous compounds include metal cations, organic amines, organic quaternary ammonium bases, fluorine ions and metal complexes. For instance, aluminosilicate zeolite molecular sieves are commonly synthesised from basic solutions. In view of the presence of OH⁻ in the solution, this implies that cations must coexist as well. Standard cations which are found in the synthesis of aluminosilicate zeolites are alkali metal cations, such as Li⁺, Na⁺, and K⁺, as well as alkaline earth metal cations, for example Ca²⁺ and Ba²⁺. This diversity of cations acting as templates results in distinct structures of zeolites²⁴.

In contrast to rigid spherical inorganic cations, organic molecules or their respective cations exhibit more complicated shapes and sizes, thus allowing greater freedom of choice in the synthesis of microporous compounds. With the exception of some zeolites which are crystallized from systems containing metal cations, most microporous compounds to this day are synthesised under the effect of organic SDAs. A list of typical zeolite structures and their corresponding SDAs is available in Table 1.3²⁵. Apart from organic amines or ammoniums, other organic compounds which could also be employed as SDAs are polymers, alcohols, ketones and organic sulfur compounds⁶.

33

Framework	Type of materials	SDA	Framework	Type of materials	SDA
ABW	Li-A(BW)	Li ⁺	EUO	EU-1	Me ₃ N(CH ₂) ₆ NMe ₃
ACO	ACP-1	H2NCH2CH2NH2	FAU	Faujasite	Na ⁺
AEI	AIPO ₄ -18	Et ₄ N ⁺	FAU	SAPO-37	$Me_4N^+ + Pr_4N^+$
AEL	AlPO₄-11	Pr2NH, iPr2NH, Bu2NH	FER	ZSM-35	H ₂ NCH ₂ CH ₂ NH ₂ , pyrrolidine
AFI	AIPO ₄ -5	Et ₄ N ⁺ , Pr ₄ N ⁺ , Pr ₃ N, Et ₃ N, etc.	GME	Gmelinite	DABCO
AET	AIPO ₄ -8	Bu ₄ N ⁺ , Bu ₂ NH, Pr ₂ NH	IFR	ITQ-4	N-benzylquinuclidine
AFN	AIPO ₄ -14	t-BuNH ₂ , iPrNH ₂	KFI	ZK-5	Triethylenediamine
AFR	SAPO-40	Pr_4N^+	LTA	Linde Type A	Na ⁺
AFT	AIPO ₄ -52	$Et_4N^+ + Pr_3N$	LTA	SAPO-42	$Me_4N^+ + Na^+, Et_4N^+$
APD	AlAsO-1	HOCH ₂ CH ₂ NH ₂	LTL	Linde type L	K ⁺
AST	AlPO₄-16	quinuclidine	MAZ	Ω	$Me_4N^+ + Na^+$
ATS	MAPO-36	Pr ₃ N, Pr4N ⁺	MEL	ZSM-18	(Me ₃ N ⁺ CH ₂ CH ₂) ₃ CH
ATT	AIPO ₄ -33	Me ₄ N ⁺	MEL	ZSM-11	Bu₄N ⁺
AWO	AIPO ₄ -21	Me ₃ N, PrNH ₂	MEL	ZSM-5	Pr_4N^+ , $H_2N(CH_2)_6NH_2$, etc.
BEA	β	Et₄N ⁺	MTN	ZSM-39	pyrrolidine, piperidine
BPH	BePO-H	$Na^+ + K^+ + Et_4N^+$	MTT	ZSM-23	pyrrolidine
BPH	Linde Q	K ⁺	MTW	ZSM-12	Et₄N ⁺
CFI	CIT-5	N-methylsparteinium	MWW	MCM-22	hexamethylenediamine
CHA	SAPO-34	Et ₄ N ⁺ , PrNH ₂	OFF	Offretite	$K^+ + Me_4 N^+$
-CLO	Cloverite	quinuclidine	RHO	Rho	$Na^+ + Cs^+$
DFO	DAF-1	$\dot{H}_2N(CH_2)_{10}NH_2$	RUT	Rut-10	Me ₄ N ⁺
DFT	DAF-2	DEA	SBE	UCSB-8Co	$H_2N(CH_2)_6NH_2$
DOH	Dodecasil-1H	pyrrolidine, MeNH ₂	SBS	UCSB-6GaCo	$H_2N(CH_2)_6NH_2$
EMT	EMC-2	18-crown-6	VFI	VPI-5	Pr ₂ NH
ERI	Erionite	$Na^+ + K^+ + Me_4N^+$	ZON	ZAPO-M1	MeN ⁺
ERI	Alpo ₄ -17	cyclohexylamine, piperidine			

Table 1.3: Common zeolite structures and their respective SDAs²⁵.

In a similar manner to inorganic bases, the main function of organic bases during the synthesis of microporous compounds is adjust pH and compensate charge. In contrast to inorganic bases, organic bases also assume a templating or structure-directing role in the formation of the framework of these compounds. Because organic templates exhibit divergent sizes and structures, they end up playing distinct roles under different reaction conditions. Five fundamental effects summarize the role of organic templates, namely: (1) the true templating effect; (2) the structure-directing effect; (3) the space-filling effect; (4) the charge-balancing effect; and finally (5) other effects²⁴. Other effects involve the function as suppressing agent, preventing the introduction of inorganic cations and behaving as complexing agent.

1.3 SAPO Materials

Before the development of Cu-containing chabazite (CHA)-type materials for SCR applications, H-SAPO 34, a silicoaluminophosphate material isostructural to SSZ-13 zeolite, has delivered outstanding results as a commercial methanol-to-olefin (MTO) catalyst^{26,27}. A high selectivity of >80% to light olefins (C₂-C₄) with close to 100% conversion of methanol characterises this material, due presumably to its shape selective catalysis by small pore entrance and its mild acidity²⁸. Nevertheless, one of the main issues with SAPO-34 catalysts concerns their rapid deactivation and, consequently, short lifetime as a result of coke formation during MTO conversion^{29–33}. On the other hand, SAPOs with Cu²⁺ cations in extra-framework positions have been found to possess exceptional activity in SCR of NO with NH₃, a crucial step for diminishing pollution caused by lean burn engines^{34–36}. SAPO-34 and -18, as well as other materials exhibiting the CHA and AEI zeolite topology types, are at the center stage of research for SCR^{37,38}. Given the fact Cu-SAPO-34 and Cu-SAPO-18 lose crystallinity and therefore activity under hydrothermal treatment at 900°C, further work still remains to be done regarding their hydrothermal stability³⁹.

1.3.1 SAPO-34

SAPO-34 {e.g. mR[Al₁₇P₁₂Si₇O₇₂] (R = morpholine, tetraethylammonium hydroxide, triethylamine, diethylamine, etc.) as one possible composition} possesses 3-dimensional interconnected channels featuring circular 8-ring openings. With the CHA zeolite framework type, SAPO-34 has a hexagonal lattice system built up by two types of composite building units, namely *d6r (t-hpr)* and *cha (t-cha)*¹². These units, the framework and its cell parameters are available in Figure 1.5. For the synthesis of SAPO-34, there is a wide array of templates which can be used, such as tetraethylammonium hydroxide (TEAOH), morpholine, triethylamine (TEA) and diethylamine (DEA)⁴⁰⁻⁴⁴.



Figure 1.5: Cell parameters, composite building units and CHA-framework of SAPO-34 with a hexagonal lattice system¹².

1.3.2 SAPO-18

SAPO-18, another silicoaluminophosphate material with a framework distinct to that of SAPO-34, is also employed for the conversion of MTO and manifests likewise an elevated selectivity of light olefins^{45,46}. In contrast to SAPO-34, it exhibits a lower deactivation rate due to larger cages, more rigid double-6-ring arrangement, reduced acid strength and inferior strong acid sites density on its surface⁴⁷. Furthermore, the synthesis of SAPO-18 is cheaper and simpler than that of SAPO-34 because of lower toxicity and cost of the utilized organic template, specifically *N*,*N*-Diisopropylethylamine (C₈H₁₉N)⁴⁷. Still, a major disadvantage for SAPO-18 is that its synthesis is time-consuming, with crystallization lasting 7 to 8 days^{38,48}. As for its crystal structure, SAPO-18 manifests the AEI zeolite framework type and its literature cell parameters indicate an orthorhombic lattice system⁴⁹. Besides, only the composite building unit *d6r (t-hpr)* constitutes the framework. Details of SAPO-18 can be gathered
from Figure 1.6.



*Figure 1.6: Cell parameters, composite building unit and AEI-framework of SAPO-18 with an orthorhombic lattice system*⁴⁹.

1.3.3 SAPO-56

Another nanoporous material of interest is SAPO-56, which so far has been reported to possess strong CO₂ adsorption capacity and readily regenerated properties, with the potential of commercial application as an adsorbent and catalyst⁵⁰. Owing to the fact that SAPO-56 features quite active acid sites and small pores ideal for uptake of Cu²⁺ cations, it is speculated that its small metal exchanged crystals may also exhibit considerable NH₃-SCR activity for an effective abatement of $NO_x^{51,52}$. In comparison to SAPOs with CHA-framework and other zeolites from a recent study by Bacsik et al., SAPO-56 was found to have the highest CO₂ working capacity (total uptake of 2.07 mmol*g⁻¹)⁵³. For the purpose of biogas upgrading, SAPO-56 manifests an elevated CO₂-over-CH₄ selectivity between 20 and 30, which is comparable to that of CHA-framework containing SAPOs⁵³. As for its synthesis, SAPO-56 can be obtained via microwave heating at 150°C and 250 psi with N,N,N',N'tetramethyl-hexane-1,6-diamine (TMHD) as the template⁵⁴. As opposed to conventional heating, microwave heating results in quicker crystallization, phase selectivity, narrow particle size distribution, abundant nucleation, morphology and size control, as well as fast and uniform heating^{55–57}. Furthermore, SAPO-

56 is assigned to the AFX zeolite framework type; the AFX-framework is composed of three composite building units, these being *d6r (t-hpr)*, *gme (t-gme)* and *aft (t-aft)*⁵⁸. The cell parameters below in Figure 1.7 indicate a hexagonal lattice system.



Figure 1.7: Cell parameters, composite building units and AFX-framework of SAPO-56 with a hexagonal lattice system⁵⁸.

1.3.4 SAPO-35

SAPO-35, another small-pore silicoaluminophosphate, is known to present high activity and selectivity as a catalyst in the MTO process^{59–61}. Unfortunately, SAPO-35 shows rapid deactivation in this process due to the deposition of high molecular weight hydrocarbons inside the microporous

cavities. With the pores' entrances blocked, reactants and intermediates are not able to reach active sites⁶². Despite this, the material has found application as an adsorbent or catalyst in other processes and reactions^{45,50,63}. For the hydrothermal synthesis of SAPO-35, hexamethyleneimine (HMI) can be used as the organic template. *Pinilla-Herrero et al.* have found that glucosamine as an additive in the synthesis gel exhibits a crystal growth modifier effect, but does not generate mesopores as expected⁶². Last but not least, SAPO-35 possesses the LEV zeolite framework type, which consists of the two composite building units *d6r (t-hpr)* and *lev (t-lev)*⁶⁴. These and the cell parameters, which correspond to a hexagonal lattice system, can be observed in Figure 1.8.



Figure 1.8: Cell parameters, composite building units and LEV-framework of SAPO-35 with a hexagonal lattice system⁶⁴.

1.4 Alternative Zeotype Materials

As a class of molecular sieves, magnesium aluminophosphates (MAPOn) feature magnesium atoms that have substituted a portion of the aluminium atoms in the framework. Consequently, acidic hydroxyl groups are generated which influence the catalytic and adsorptive properties of these zeotype materials⁶⁵. In the case of MAPO-39, this small pore molecular sieve is characterised by its ATN topology⁶⁶. McCusker et al. reported that it possesses a body centered tetragonal unit cell with a = 13.09 Å and c = 5.18 Å. Furthermore, MAPO-39 contains a 1-dimensional channel system with an 8 oxygen ring pore opening, having a pore diameter of 0.4 nm⁶⁷. Akolekar and Kaliaguine published the hydrothermal synthesis procedure of the molecular sieve, stating a gel of the following composition which was used for crystallization in a Teflon-coated autoclave at 423 K for 96 h⁶⁸:

• *n*-Pr₂NH : 0.40 MgO : 0.80 Al₂O₃ : 1.02 P₂O₅ : 41 H₂O.

As for MeAPO compositions, these display intermediate framework charge densities (FWCDs) that lie between that of the endmember compositions, the neutral AIPO and the charged Me²⁺-P⁵⁺-O frameworks. The latter case is characterised by the formulation [Me²⁺P⁵⁺O₄]⁻ with a FWCD corresponding to that of Si/Al = 1 for aluminosilicates⁶⁹. Broach et al. describe the synthesis of new MeAPO materials of moderate FCWD by utilizing the structure directing agents diethyldimethylammonium hydroxide (DEDMAOH) and ethyltrimethylammonium hydroxide (ETMAOH). This has led to the production of novel materials. such as ZnAPO-57 in the diethyldimethylammonium (DEDMA) system after crystallization at 448 K for 37 h and ZnAPO-59 after crystallization at 423 K for 84 h in the ETMA system. Both feature unique framework topologies belonging to the ABC-6 net family⁶⁹. Any modification of the SDA/H₃PO₄ and Si substitution in the SDA synthesis system results in materials with distinct FWCD and framework topologies.

Aluminophosphate molecular sieves (AIPO₄-*n*) feature a univariant framework composition ($n_{AI} / n_P = 1$), substantial structure diversity and topologies that also appear in zeolites, as well as a large range of pore sizes and volumes, which in the upper end includes the 18-membered ring material

VPI-5¹⁴. Further known aluminophosphate structures exhibiting different pore diameters include AIPO₄-5, AIPO₄-11, and AIPO₄-21²³. This class of compounds possess one-dimensional chain, two-dimensional sheet, and three-dimensional open-framework structures²³. These materials also have neutral frameworks, and for this reason are not capable of ion-exchange. On the other hand, the surface selectivity presents itself as weakly hydrophilic. In addition, they possess outstanding thermal (1000°C) and hydrothermal (600°C) stability¹⁴. In contrast to aluminosilicate zeolites, which are typically synthesised under alkaline conditions, the reactant gel of the AIPO₄-*n* class generally exhibits a pH value that is nearly neutral or marginally acidic²³.

1.5 Core-shell and Hybrid SAPOs/Zeolites

1.5.1 Overview

Zeolites, which are applied in heterogeneous catalysis as well as for purification and separation purposes, do experience limitations with their small microporous channels owing to the size similarity between the micropore diameter and implicated guest molecules⁷⁰. As key players of catalytic and separation processes, zeolitic molecular sieves possess uniform three-dimensional nano-channels with distinct distribution and strength of acid sites⁷¹. Chemical reactions are influenced by external crystal surfaces, internal channels with divergent acid strengths and shape sieving behaviors⁷². Despite the low concentration of external surface active sites, their role in catalytic reactions cannot be considered minor since they are responsible for diffusional restrictions on reactants that stream into active sites in micropores⁷³.

The idea behind adjusting the diffusion path length of a zeolite is to change the morphology or crystal size, subject to specific preparation requirements⁷⁰. Hierarchical pore systems, which have been produced to decrease diffusion path lengths in the micropores of available zeolites, have garnered considerable interest^{74,75}. The reduction of diffusion path lengths in zeolites can be achieved via the inclusion of a meso- or macropore system in a zeolite crystal, or by diminishing the crystal size⁷⁶.

By modifying the external surface area of zeolites, attempts have been carried out to improve their selectivity properties and reactivity⁷². To achieve a reasonable acid distribution and generate mesopores, functionalization of the external surface of zeolites has been performed via steaming, acid leaching, element surface modification, etc⁷⁷. Nevertheless, a reduction in the effective diameter of pore openings and hence a decline in catalytic activity may come as a result of species deposition and partial damage by using the aforementioned techniques. In order to attain the catalytic properties which are desired, an alternative strategy for modifying the surface structure has been suggested through the growth of a continuous shell over core crystals⁷². In this situation, a shell which oversees the functionality and stability of the composite also regulates access to a core with distinct properties⁷⁸. However, it is necessary to identify the right synthesis conditions for the coexistence of the shell and core. Complementary requirements, such as the pH value of the reactant gel, may be in stark contrast for the core and shell, and can therefore hinder the formation of the composite.

1.5.2 ZSM-5/SAPO-34 Composite

Zheng et al. have reported a novel synthesis route for hierarchical pore zeolite composites with a core-shell structure by utilizing a commercial ZSM-5 zeolite powder as silica source and core for the crystal growth of a SAPO-34 shell⁷⁹. Because ZSM-5 framework has low stability in acid solutions and thus undergoes partial depolymerization during the subsequent hydrothermal synthesis, it can be used as a seed crystal from which SAPO-34 builds up. The extraction of silicon and/or aluminium species from the ZSM-5 framework not only benefits the generation of SAPO-34, but it also facilitates the formation of a hierarchical pore system in zeolite composite crystals⁷⁰.

1.5.3 ZSM-5/SAPO-11 Composite

Zeolite ZSM-5 is known to manifest excellent activity for hydrodesulfurization, as well as light alkane and alkene aromatization^{80,81}.

Another silicoaluminophosphate, SAPO-11, is commonly employed for the isomerization of C_4 - C_7 hydrocarbons in the production of gasoline featuring a high research octane number (RON)⁸². The material also contributes to the dewaxing process responsible for high quality diesel and lube oil basestocks by means of isomerization of long-chain alkanes as a result of its elevated hydroisomerization activity⁸³.

Zeolites have uniform three-dimensional nano-channels with characteristic strength and distribution of acid sites⁷¹. Their external crystal surfaces, internal channels with different acid strengths and shape sieving behaviours affect the outcome of chemical reactions⁷². In addition, external surface active sites play an important part in catalytic reactions due to the diffusional restrictions they impose on reactants that enter active sites in micropores⁷³. A single zeolite, such as SAPO-11 with its unique characteristics, does not necessarily exhibit desulfurization activity because of the factors mentioned above.

For this reason, a ZSM-5/SAPO-11 composite with an optimized catalyst composition is expected to deliver a balanced desulfurization, aromatization and hydroisomerization performance, therefore improving the upgrading process of fluid catalytic cracking (FCC) gasoline⁸⁴. In comparison to mechanical mixtures, the composite features more mesopores which facilitate substance diffusion as well as favourable acidity distribution that improves the synergetic effect between Lewis and Brønsted acid sites. Fan et al. have shown that these two variables can considerably boost the reaction performance of the composite-derived FCC gasoline hydro-upgrading catalyst⁸⁴.

1.5.4 ZSM-5/SAPO-5 Composite

A relatively high hydrothermal stability characterises core/shell structure micro-microporous zeolite composites. As opposed to ZSM-5, SAPO-5 possesses larger pores and weaker acidity⁸⁵. However, it should be pointed out that the acid strength of SAPO-5 is considerably greater than that of analogous AIPO₄ materials. In addition, SAPO-5 manifests a strong selectivity of light olefins when assessing its efficiency for catalytic conversion of heavy oil in a

catalytic cracking unit⁸⁵. Benefits from a ZSM-5(core)/SAPO-5(shell) composite can be envisaged, since the shell zeolite does not only offer weak acidity and larger pores to the core zeolite, but also aids in diminishing the diffusion distance of intermediate products. Depending on the framework properties of the core and shell zeolites, multiple kinds of zeolite composites can be created via isomorphic substitution, epitaxial growth or overgrowth⁸⁵. When the shell and core share similar frameworks, for instance ZSM-5/silicalite, it is possible to produce composites by means of isomorphic substitution of framework atoms. Although this procedure can be put into practice, only few zeolites are compatible for the purpose in discussion⁸⁵.

1.5.5 Beta/SAPO-11 Composite

Currently, there is not extensive research on composite molecular sieves for the isomerization of long-chain alkanes. Because diffusion and reaction mechanisms of *n*-alkanes with distinct numbers of carbon atoms behave differently on catalysts, chemical and physical properties of composite molecular sieves impact strongly on the isomerization performance⁸⁶. Beta, a large-pore high-silica crystalline aluminosilicate zeolite, presents itself as a superb catalyst for light paraffin isomerization reactions⁸⁷. On the other hand, SAPO-11 exhibits greater performance than other zeolites in decreasing the pour point of diesel due to its medium acidity and optimal pore size⁸⁸. Taking all this into account, a composite molecular sieve of Beta and SAPO-11 constitutes of the most promising bifunctional catalysts in the field of one hydroisomerization reactions⁸⁶. Employing Beta as a seed for crystallization, Wang et al. reported the synthesis of a Beta(core)/SAPO-11(shell) composite molecular sieve via the hydrothermal method⁸⁹. Under mildly alkaline conditions, Zhang et al. mention the synthesis of a SAPO-11/Beta composite molecular sieve with a mosaic structure⁹⁰.

1.6 Synthesis of ZSM-5/SAPO-34 and SAPO-34/ZSM-5 Composite Systems

1.6.1 Synthesis Procedure Scheme

Razavian and Fatemi have reported the synthesis of ZSM-5/SAPO-34 binary nanostructured composites by utilizing two different sequential crystallization procedures depending on the core and shell materials⁷². Both procedures are portrayed in Figure 1.9. A more effective procedure has been suggested to preserve SAPO-34 crystals in the potent basic precursor media of ZSM-5 which is employed for generating an innovative bi-phase SAPO-34/ZSM-5 (core/shell) zeolite composite⁷². Even though ZSM-5 and SAPO-34 zeolites do not exhibit chemical compatibilities nor comparable framework compositions, the stability of SAPO-34 in an aggressive synthesis media was ensured by means of pre-treatment. By combining valuable physicochemical properties of these two kinds of zeolites with the structural codes CHA and MFI, a hierarchical composite can be produced with optimized surface properties and modified distribution of active centers⁷². The catalytic, adsorptive and sieving funtions of both flanking structures are merged and assembled as desired, thus allowing a greater application range for these materials.

The following compounds in Figure 1.9 are abbreviated as follows: tetraethyl orthosilicate (TEOS), aluminium isopropoxide (AIP), ortho-phosphoric acid (H₃PO₄), hydrochloric acid (HCl), diethylamine (DEA), polyethylene glycol (PEG), tetraethylammonium hydroxide (TEAOH) and tetrapropylammonium bromide (TPABr)⁷². Concerning the top synthesis procedure scheme of ZSM-5/SAPO-34, it shows how the binary composite is formed by way of a sequential crystallization. To begin with, a seeding method is used involving silicalite-1 seeds as SDA for the synthesis of ZSM-5 core crystals. After preparing the homogeneous reactant gel, it is placed in an autoclave and heated for crystallization. Meanwhile, a SAPO-34 precursor gel is produced in a second step. The SAPO-34 gel and ZSM-5 slurry are blended, followed by hydrothermal treatment in an autoclave. As-synthesised product crystals are

then subjected to centrifuging and washing with deionised water. Afterwards, they are dried and calcined⁷².

Regarding the bottom synthesis procedure scheme of SAPO-34/ZSM-5, the composite is generated via one-step crystallization of ZSM-5 pre-reacted synthesis gel and pre-treated SAPO-34 powder. Here, a precursor gel for the synthesis of the SAPO-34 powder is prepared and then undergoes hydrothermal treatment. This is followed by centrifugation and washing of the final solid product for its recovery. Next, the crystals are subjected to drying and calcination. The calcined powder is then ion-exchanged twice with TPABr propanolic solution, with the resulting product designated as TPA-SAPO-34⁷². The aim of the ion exchange with TPABr is to protect the SAPO-34 crystals from the strong basic synthesis medium of the composite reactant gel. In the meantime, a ZSM-5 reactant gel is prepared and then heated in an autoclave for pre-crystallization. Next, TPA-SAPO-34 is transferred into the pre-reacted ZSM-5 under stirring, with the mixture being hydrothermally treated in an autoclave in the next step. Lastly, the solid as-synthesised compound is recovered by means of centrifugation and washing with deionised water, followed by drying and calcination⁷².



Figure 1.9: Schemes of ZSM-5/SAPO-34 (top) and SAPO-34/ZSM-5 (bottom) composite overall synthesis procedure⁷².

1.6.2 Synthesis Parameters and XRD Pattern Results

The synthesis parameters used by Razavian and Fatemi for composite molecular sieves are listed in Table 1.4⁷². In this case, the designations ZS and SZ represent respectively series of ZSM-5/SAPO-34 and SAPO-34/ZSM-5 composites. To determine the crystalline structure of the mentioned composites, XRD patterns of these synthesised samples can be observed in Figure 1.10 together with reference patterns of SAPO-34 and ZSM-5⁷². With the exception of ZS2, the distinctive peaks of CHA (2 θ° ~9.6°, 13°, 20.8° and 30.1°) and MFI $(2 \theta^{\circ} \sim 7.9^{\circ}, 8.8^{\circ}, 23.1^{\circ}, 23.9^{\circ}, and 24.4^{\circ})$ appear in all binary composites. Regarding the SZ series, the synthesis media does not seem to affect the SAPO-34 crystals considerably. It should nevertheless be pointed out that the intensity of the CHA diffraction peaks depends on the mass of SAPO-34 crystals which was weighed in⁷². As expected, the characteristic peaks of CHA for SZ1 are weaker than the ones of SZ2 due to the lower content of SAPO-34 in the synthesis procedure. In contrast, major CHA diffraction peaks in the ZS2 pattern are concealed by substantially stronger MFI signals. This last composite was meant to possess a very thin uniform layer of SAPO-34 surrounding highly siliceous ZSM-5 core crystals, which may have led to diffraction from CHA appearing undetectable⁷². Apart from this, there are no other recognizable phases in the XRD patterns. The diffraction peaks of the composites are less intense than those of the SAPO-34 and ZSM-5 standards due to the shielding effect of materials around core seeds⁷². Despite the results from XRD, the analytical technique cannot differentiate coexisting phases from core/shell assemblies. By incorporating further characterisation techniques such as scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS), it is possible to determine whether core/shell composites are available.

Table 1.4: Synthesis parameters of ZSM-5/SAPO-34 and SAPO-34/ZSM-5 composite molecular sieves⁷².

Sample	Shell/core	Mixing time (h)	Aging time (h)	Crystallization	TEAOH/DEA
	content			technique	molar ratio
	Volume ratio	ZSM-5 suspension and	SAPO-34		
		SAPO-34 precursor gel	precursor gel		
ZS1	1	1		Static condition	1/9
ZS2	6	2		Dynamic condition	9
				(8.5 rpm)	
	Weight ratio	TPA-SAPO-34 powder and	ZSM-5		
		pre-reacted ZSM-5 slurry	precursor gel		
SZ1	5.5			Static condition	1/9
SZ2	1.5			Dynamic condition	9
				(8.5 rpm)	



Figure 1.10: XRD diffractograms of SAPO-34/ZSM-5 and ZSM-5/SAPO-34 composite molecular sieves, as well as SAPO-34 and ZSM-5 standards: (a) SAPO-34, (b) SZ1, (c) SZ2, (d) ZS1, (e) ZS2 and (f) ZSM-5⁷².

1.7 Standard NH₃ Selective Catalytic Reduction

1.7.1 Overview

As by-products from combustion processes, nitric oxide and nitrogen dioxide still play a decisive role as air pollutants in urban and industrial areas⁹¹. To diminish NO_x emissions from exhausts of stationary and mobile diesel engines, selective catalytic reduction with ammonia (NH₃-SCR) for the deNO_x process is perceived as a suitable approach by which to achieve this⁹². Vanadium based catalysts have been thoroughly investigated and employed in the past as monolith converters in diesel vehicles for reduction of NO_x emissions⁹³. Nevertheless, V-based catalysts exhibit certain disadvantages, such as strong activity for oxidation of SO₂ to SO₃, poor SCR activity at low temperatures, thermal deactivation, toxicity and disposal issues⁹⁴.

In recent decades, investigation into the reduction of NO_x emissions has resulted in the industrial application of transition metal oxides and zeolite catalysts that are considerably less expensive than the noble metals employed in automotive catalytic converters^{95,96}. At the moment, Cu/Fe-zeolites outnumber considerably V-based catalysts in NH₃-SCR processes⁹⁷. Various kinds of these catalysts have been assessed, studied and eventually brought to use in the SCR industry because of their reliability and efficiency⁹⁸. Apart from this, the appearance of zeolite-based catalysts in SCR technology has also contributed to the gradual disappearance of V-based catalysts for this application^{99,100}.

Zeolite catalysts which possess the chabazite structure, specifically copper-exchanged SAPO-34 and SSZ-13, have demonstrated an elevated degree of conversion of NO_x and selectivity towards N₂, whilst at the same time being able to maintain hydrothermal stability^{1,91}. Following various spectroscopic, catalytic and computational studies, considerable progress has been achieved to explain the deNO_x reaction mechanism, as well as to clarify the formation of the adsorption complexes of NO, N₂O, and NO₂ with alkaline, alkaline-earth and transition metal extra-framework cations^{101,102}. SSZ-13 and SAPO-34 in particular, but also zeolites featuring the small-pore chabazite

(CHA) framework exchanged with copper, have been proven to exhibit remarkable resistance to elevated temperatures during the regeneration of the Diesel Particulate Filter (DPF), which is located upstream of the SCR unit¹⁰³.

Even though many studies have been carried out, unresolved issues and difference in opinions amongst researchers regarding SCR literature still remain. The main topics of concern in the chemical pathways of Standard SCR are the mechanism of Standard SCR reaction, depicted in Equation 1.5, and the function of NO oxidation reaction, appearing in Equation 1.6. The ample scope of gas compositions emitted by diesel engines and the governing operating conditions within automotive converters highlight the need to identify SCR mechanisms by modelling the kinetics behind the SCR reactions¹⁰⁴. NO comprises the bulk of NO_x generated by diesel engines. For this reason, most of the deNO_x activity takes place with the Standard SCR reaction, where NO is reduced by NH₃ in the presence of oxygen¹⁰⁴. Various research groups have been attempting to establish a mechanism for the Standard SCR reaction that is consistent with kinetic experiments involving Cu/Fe-zeolites¹⁰⁵.It remains unknown whether formation of NO₂ via the NO oxidation reaction produces an active gaseous intermediate that acts as the rate determining step (RDS) of the Standard reaction, or if NO₂ does not participate in the latter reaction as an intermediate species^{106,107}. In view of this, the quantitative characterisation of the NO oxidation is crucial in outlining the complex deNO_x chemistry that occurs in a state-of-the-art SCR converter.

$$4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O \quad \Delta H = -4.07 \times 10^5 \text{ J/mol NH}_3$$
 (1.5)

$$2NO + O_2 \longrightarrow 2NO_2 \quad \Delta H = -5.7 \times 10^4 \text{ J/mol NO}$$
 (1.6)

Besides the function of NO oxidation in Standard SCR, the exceptional oxidative nature of NO₂ makes it essential for the deNO_x aftertreatment of gas emissions¹⁰⁴. With the presence of NO₂ in the feed stream to the SCR reactor, the direction of the NO reduction is shifted towards another chemical pathway, namely the fast SCR reaction. This reaction, which can be observed in Equation 1.7, operates at a higher rate than Standard SCR and can also be detected at comparatively low temperatures¹⁰⁸. In practice, the exhaust gas travels through

a Diesel Oxidation Catalyst (DOC) before arriving at the SCR converter¹⁰⁹. The DOC consists of a platinum based catalyst, with alumina, silica, zirconium and other alternatives functioning as support materials¹¹⁰. Because of this, the DOC is a rather costly component of the aftertreatment system in vehicles¹⁰⁴. On the other hand, Olsson et al. have reported that ion-exchanged zeolite SCR catalysts are more economical than DOCs and capable of oxidizing NO to NO₂¹¹¹. By and large, there is much to gain for modelling purposes by achieving further insight into NO oxidation over novel SCR catalysts, such as Cu-CHA systems¹⁰⁴.

$$2NH_3 + NO + NO_2 \longrightarrow 2N_2 + 3H_2O \quad \Delta H = -3.78 \times 10^5 \text{ J/mol NH}_3$$
 (1.7)

1.7.2 NH₃-SCR Mechanisms

Despite standard NH₃ selective catalytic reduction (NH₃-SCR) of NO_x being thoroughly studied, there is no consensus as to its reaction mechanisms¹¹². Fundamental issues that lead to disagreement in the NH₃-SCR mechanism include: (1) whether catalytically relevant Cu/Fe species in ionexchanged zeolite catalysts exhibit a monomeric, dimeric, or even very small oligomeric cluster arrangement; (2) whether NO₂ assumes an active role in the mechanism; (3) whether the catalytic centers are subjected to redox cycling; and (4) whether both Brønsted acid sites and Cu/Fe ion sites jointly deliver the catalytic functionality¹. The reaction mechanism can be described to be of the Eley-Rideal (E-R) or Langmuir-Hinshelwood (L-H) type, depending on whether activation of NO takes place. Concerning the E-R reaction, chemisorbed NH₃ reacts with weakly-bound NO to generate intermediates that then lead to N₂ via decomposition, whereas in the case of the L-H mechanism, NO must be converted into strongly-bound species (for instance NO₂, nitrite or nitrate moieties) before reacting with ammonia¹. Nevertheless, a reaction ratio of $NH_3/NO = 1/1$ and an oxidation state mismatch of nitrogen atoms in the reactants (in other words +2 in NO and -3 in NH₃) make it necessary for active centers to be reduced during the E-R reaction. Because of the continuous turnover, reduced active centers must be oxidized by O₂. In effect, the catalytic

centers involved in the E-R mechanism must be linked to redox steps¹. This last aspect is also valid for the L-H mechanism. But in addition to this, NO activation accompanies catalytic center reduction.

A standard SCR mechanism for metal-exchanged zeolite catalysts proposed by Iwasaki, which in turn is akin to another one for V₂O₅-based catalysts, can be observed in Figure 1.11¹¹³. Here, a standard L-H mechanism is conjugated to redox of catalytic centers under the following premises: (1) reactive ammonia participates as a NH₄⁺ species; (2) reactive NO_x is present as an NO₂(ads) species which is generated by NO oxidation due to extra lattice oxygen (ELO); and (3) a dual-site intermediate undergoes decomposition to form N₂. Nevertheless, arguments reported by Beale et al. suggest that such a mechanism is inconceivable for Cu-CHA catalysts¹.



Figure 1.11: Adapted portrayal of the catalytic cycle for standard SCR reaction over metal-exchanged zeolite catalysts. Acid sites correspond to Lewis or Brønsted sites at ion-exchanged metal or free proton sites. Redox sites are represented by isolated or binuclear oxo-metal ion-exchanged sites^{1,113}.

An alternative SCR mechanism, which is portrayed in Figure 1.12, has been proposed by Paolucci et al. where a nitrosoamide-like complex is implicated in the reducing half-cycle and an ammonium nitrite-like complex participates in the oxidizing half-cycle of a turnover¹¹⁴. In this study, a naked Cu²⁺ monomer is assumed to be positioned in the faces of the 6-rings (6R) in the zeolite structure with two AI T sites as the active center. This is the most probable scenario for a high-temperature kinetic regime, but not necessarily the case at low reaction temperatures¹. In addition, NH₄⁺ is employed in the proposed mechanism as a decisive reactant species in the oxidizing half-cycle. Nevertheless, there are reports indicating that NH₄⁺ is not particularly reactive^{36,115}. Furthermore, a conflicting point amongst some mechanistic models is the manner in which NO is activated, and if the formation of NO₂ is actually decisive and even a rate-limiting step for standard SCR¹.



Figure 1.12: Adapted SCR cycle proposal over Cu-SSZ-13 (isostructural to Cu-SAPO-34) at 473 K. Oxidized Cu (top) and its reduced (bottom) halves of the redox cycle are divided by the dotted line^{1,114}.

With the help of FTIR, Szanyi et al. have described the formation of NO⁺ species during NO chemisorption on Cu-SSZ-13¹¹⁶. By employing ¹⁵N solid-state MAS-NMR, the generation of a Cu⁺-NO⁺ complex was also corroborated¹¹⁷. After being formed, it is possible that NO⁺ moves to extra-framework cationic sites to counteract negative framework charges¹¹⁸. One way or another, it is very plausible that this species reacts with H₂O to form HNO₂, which can then be succeeded by formation of ammonia nitrite that then

decomposes to N₂. Given these conditions, Kwak et al. have come up with a simplified standard SCR mechanism that is illustrated in Figure 1.13^{117} . Nonetheless, NO⁺ can only be viewed in the absence of NH₃¹¹⁵. As a consequence, there are two possible situations under SCR conditions: (1) NO⁺ is consumed instantly after being generated, and therefore remains below the detection limit of FTIR; and (2) it does not participate in the presence of NH₃. Because of the constraints of the FTIR technique, the proposed mechanism cannot be safely ratified¹.



Figure 1.13: Adapted mechanism proposal for SCR of NO with NH₃ over Cu-SSZ-13 comprising an NO⁺ intermediate^{1,117}.

1.7.3 Hydrothermal Stability during NH₃-SCR of NO_x

Acid rain, haze and photochemical smog is caused by different kinds of pollutants, but mainly by NO_x from diesel exhaust engines¹¹⁹. To boost air quality, it is vital that NO_x emissions are diminished. NH₃-SCR of NO_x is currently acknowledged as one of the most promising techniques for NO_x emission control of diesel engines¹²⁰. To keep up with regulations, the use of lean burn diesel engines depends on the efficient reduction NO_x and particulate matter (PM), with these being primary diesel exhaust components. A diesel oxidation catalyst (DOC) and diesel particulate filter (DPF) are employed in a

conventional NH₃-SCR after-treatment system to eliminate CO, unburned hydrocarbons and particulate matter upstream of the SCR catalyst¹²¹. Because of the erratic operating conditions present in diesel engines, as well as the fact that the DPF regeneration needs to be reproduced by intermittently increasing the exhaust temperature, superb catalysts should conform to a set of key requirements: satisfactory SCR activity covering a broad operating temperature range, exceptional hydrothermal stability and elevated selectivity for N₂¹¹⁹. This is due to the fact that the DPF regeneration might expose the SCR catalyst to temperatures above 650°C and moisture from the feed, leading to the zeolite framework structure being damaged and the catalyst being deactivated. As a result, resilience towards hydrothermal aging is decisive for NH₃-SCR catalyst application¹²¹.

For the NH₃-SCR reaction, copper-based zeolites have been proposed to be efficient catalysts, with Cu-ZSM-5 being claimed to have the most potential^{122,123}. Nevertheless, a distinct drop in NH₃-SCR activity takes place after Cu-ZSM-5 is subjected to high temperature hydrothermal aging, which correlates to a framework collapse of the catalyst¹²⁴. Cu-CHA catalysts such as Cu-SAPO-34 and Cu-SSZ-13, which are supported on microporous zeolites manifesting a ~0.38 nm pore size, are currently at the center of debate owing to their higher NH₃-SCR activity and greater hydrothermal stability in contrast to alternative large or mesopore Cu-based zeolite catalysts¹²⁵. Over a temperature span of 250 to 450°C, NO conversion in reaction trials with Cu-CHA catalysts lies between 90 and 100%. In fact, despite hydrothermal aging of the catalysts at 800°C, conversion remains above 80%¹²⁶. This is also valid for Cu-SAPO-34 and Cu-SSZ-13¹²⁵. The dealumination product Al(OH)₃, which features a calculated kinetic diameter amounting to 5.03 Å, is prone to be confined in the small pores. Consequently, dealumination is inhibited while the hydrothermal aging process takes place¹²⁵.

In the case of Cu-SAPO-34, Niu et al. have reached the conclusion that hydrothermal resistivity and NH₃-SCR activity rely upon the stability of the structure, framework pore properties, acidity, and distribution of Cu species. Its pore volume, surface area, and structure crystallinity were found to rise from 500 to 700°C whilst calcining, to then drop at 800°C¹¹⁹. A Cu-SAPO-34 catalyst with a Cu loading of 3.44 wt% was identified to exhibit excellent NH₃-SCR

activity after calcination at 700°C¹¹⁹. After exposing the aforementioned catalyst to hydrothermal aging treatment at 800°C for 16 h, it was also established that it can achieve over 90% NO_x conversion from 225 to 400°C. For that reason, the catalyst appears to have great potential for industrial purposes¹¹⁹. According to results from Wang et al., both Cu-SSZ-13 and Cu-SAPO-34 could retain their performance after being exposed to hydrothermal aging at 750°C for 16 h. Nevertheless, Cu-SSZ-13 suffered a considerable loss in SCR performance, active Cu sites and crystallinity after hydrothermal aging at 800°C for 16 h. In the case of Cu-SAPO-34, not only did its activity not fall with identical hydrothermal aging conditions, but in fact its low-temperature NO conversion improved¹²¹. Migration of residual surface Cu from the initial synthesis into the SAPO-34 pores during high temperature treatment is thought to be the underlying cause, since it brings about the generation of further isolated Cu²⁺ sites.

Distinct types and locations of Cu structures have been detected on Cu-CHA catalysts, for instance isolated Cu²⁺, Cu⁺, Cu dimers (Cu-O-Cu)²⁺, Cu_xO_v clusters, and CuO particles^{125,127}. These Cu species have been discovered by Kim et al. to possess varying resistances with regard to the hydrothermal aging process. It was further determined that the Cu²⁺ species in the D6R unit of the framework is more stable than the Cu species located at the CHA sites, prompting the assumption that hydrothermal aging of Cu-SSZ-13 catalysts is mainly caused by CHA sites^{121,128}. Niu et al. have recognized three types of Cu species on Cu-SAPO-34, including isolated Cu²⁺, CuO and Cu⁺ ions. Because of hydrothermal aging at 750°C for 16 h, migration of CuO on the external surface to isolated Cu²⁺ in the cages of Cu-SAPO-34 has raised the amount of active sites. Moreover, CuO did not aggregate and generate bigger clusters. As a consequence, the aged Cu-SAPO-34 catalyst with 3.44 wt% Cu displays superior NH₃-SCR performance in contrast to the fresh version of the catalyst¹¹⁹. Furthermore, results of kinetic studies suggest that the apparent activation energy of the fresh Cu-SAPO-34 sample is higher than that of the aged one. On balance, the higher NH₃-SCR activity and the elevated hydrothermal stability for the Cu-SAPO-34 catalyst is due to the crystallinity, acidity, the migration of CuO to isolated Cu²⁺ during NH₃-SCR and maintenance of the latter species, and the small activation barrier¹¹⁹.

1.8 Alcohol-to-Olefins Processes

Polymer production relies strongly on light olefins as raw materials, for example propylene and ethylene^{129,130}. Nevertheless, stricter environmental legislation and elevated prices of crude oil have led to greater endeavors in developing novel and upgraded catalytic technologies operating on alternative feedstocks, e.g. methane and biomass. Out of the investigated processes, the conversion of alcohols, such as ethanol and methanol, to light olefins has attracted considerable attention^{131,132}. It is possible to obtain methanol from synthesis gas (CO + H₂), which in turn can be generated from virtually any gasifiable carbon source, for instance coal, biomass, natural gas and agricultural waste¹³³. In 1976, the methanol-to-olefins (MTO) process was discovered and further optimized with the introduction of SAPO-34 by Union Carbide^{129,134}. Moreover, the ethanol-to-olefins (ETO) process has come under the spotlight due to interest in its full utilization in the generation and application of bio-ethanol, which can be produced in great volumes from state-of-the-art lignocellulosic biorefineries^{129,135}.

Numerous protonated zeolites or zeotype materials can effectively catalyse ETO and MTO processes. SAPO-34, with its network of large cavities (6.7 Å × 10.9 Å) linked via small windows (3.8 Å × 3.8 Å), is a classic industrial MTO catalyst that exhibits up to 80% total carbon yield of ethylene and propylene¹³⁶. Furthermore, the CHA framework is one of the exceptional zeotype topologies where both the silicoaluminophosphate (SAPO-34) and aluminosilicate (SSZ-13) analogues can be easily produced. In the case of SSZ-13, it has been documented to exhibit greater acidity than SAPO-34¹³⁷. Because of this, SSZ-13 has been reported to have a more elevated production rate of olefins and to retain aromatics in the catalyst pores, resulting in a lower optimal temperature of operation¹³⁸.

Novel and optimized catalyst materials can be developed more efficiently by understanding how reaction mechanisms and associated deactivation pathways work during catalytic processes. It is of general agreement that the MTO reaction adheres to the hydrocarbon pool (HCP) mechanism, by which

methanol is added to an organic scaffold^{139,140}. In addition, it has been established that supplying the catalyst H-ZSM-5 with ethanol as feed delivers a product range nearly identical to that of the MTO process¹⁴¹. In view of this, it has been hinted that the ETO process follows reaction pathways closely related to the HCP mechanism¹⁴². Analysis has revealed that, even though ETO yields more ethyl-substituted molecules than the MTO process, the trapped byproducts within the zeolite channels after ETO are very much alike to those originating from the latter^{143,144}. The zeolite activity and the generation of specific hydrocarbon species depend on an array of factors, in particular size of cages and channels of molecular sieves, reaction conditions, and acid site strength and density^{140,145}. Nevertheless, active HCP species have been found to consist mostly of alkylated benzene molecules and their protonic analogues^{145,146}. What is more, bulkier aromatics are promptly formed from active species in SAPO-34, leading to obstructed active sites and inhibited diffusion of both reactants and products^{147,148}. As a result, shifts in activity and selectivity may come about from coke build-up weakening catalyst performance¹⁴¹.

1.9 Project Aims and Objectives

As stated previously, microporous CHA zeolitic materials have been recognised as promising catalysts for NH₃-SCR reactions. However, the stability of their structural properties and crystallinity remain an issue after extended time spans. The thesis seeks to address the synthetic aspects and gel chemistry of these small pore zeolitic materials. For this purpose, combinations of SAPO-34 and shell@core type synthesis methods that include SAPO-34, SSZ-13, and silicalite-1 will be studied in order to establish connections between structural properties and stability of shell@core type nanoporous systems. This will be achieved with the assistance of laboratory-based characterisation techniques, with X-ray diffraction (XRD) as the main analysis tool; other techniques include SEM, EDS, XPS, UV-Vis, infrared and solid-state NMR spectroscopy.

In chapter three, SAPO-34 synthesis methods and its gel chemistry will be investigated to enhance directed incorporation of silicon into the zeolite framework and improve stability. The effect of variation of Si-species, its molar ratio in the reactant gel composition, order of addition of reactants, and product recovery methods will be assessed to determine the impact on the yield, phase purity, morphology and the extent of silicon incorporation on framework sites of the products. Furthermore, samples are to undergo a series of calcination runs at 550, 700 and 900°C to observe how their stability and crystallinity change.

In chapter four, shell@core synthesis combinations for silicalite-1@SAPO-34 compositions are to be carried out to understand the underlying gel chemistry and improve the stability of these materials. Modification of the surface structure of SAPO-34 will be targeted by growing a continuous hydrophobic silicalite-1 shell over SAPO-34 core crystals which stops water from entering the core during SCR while not altering the desired properties. To generate these shell@core compounds, SAPO-34 will be used as seed crystal in silicalite-1 reactant gels under various synthesis parameters and proportions.

In chapter five, shell@core synthesis combinations with SSZ-13, an aluminosilicate material which is isostructural to SAPO-34 zeolite and is also utilised in SCR and MTO catalysis, will be studied to elucidate the gel chemistry involved. Alteration of the surface structure of SSZ-13 will be attempted by generating a continuous hydrophobic silicalite-1 shell over SSZ-13 core crystals for the same reasons as SAPO-34. To establish if an isostructural shell can be grown more easily over a core with the same framework, hydrothermal synthesis of SSZ-13@SAPO-34 materials is to be pursued by placing SAPO-34 seed crystals into an SSZ-13 reactant gel. Moreover, recrystallization of SSZ-13 will be tested from a CHA to an MFI zeolite topology, in effect ZSM-5, to determine the possibility of recrystallizing the framework of an SSZ-13 shell to an MFI topology in SSZ-13@SAPO-34 materials.

On the whole, variations of gel composition, order of addition of reactants and product recovery method of SAPO-34, and shell@core type synthesis methods involving SAPO-34, SSZ-13, and silicalite-1 will be researched in this project to have a better understanding of the gel chemistry. Via laboratorybased characterisation techniques, it will be possible to determine how the gel

chemistry impacts upon the structural properties and stability of these nanoporous systems.

Chapter 2: Experimental Techniques and Methodologies

2.1 Chapter Overview

In this chapter, the experimental techniques and methodologies employed in this thesis are presented. The chapter begins by explaining the hydrothermal synthesis technique utilised for zeolite synthesis and goes further into depth describing the steps for the synthesis strategies and their differences. Furthermore, the analytical techniques for the characterisation of the zeolite samples are discussed. This includes an overview of the underlying principles and advantages for each analytical technique. The steps and parameters involved in these techniques are also laid out.

2.2 Hydrothermal Synthesis Technique

From a historical point of view, the hydrothermal method for the synthesis of zeolites first consisted of a mixture of reactive alkali metal cations with aluminosilicate gels at an elevated pH value, which would be crystallized under a modest pressure and temperature. Hydrothermal synthesis has since evolved and currently also covers crystallization of aluminosilicate/metalosilicate gels under more extreme pressures and temperatures. Even though other synthesis routes for zeolite crystallization have been discovered, such as the vapour phase crystallization method and the steam assisted method, the standard hydrothermal method remains widespread to this day.

It is understood under hydrothermal synthesis that product formation takes place in an essentially aqueous medium¹⁴⁹. To perform this synthesis method, a zeolite precursor needs to be formulated which contains silicon/aluminium/phosphorus sources, a structure directing agent, water and, if required, a source of alkali metal cation. The composition of the precursor is decisive for what kind of zeolite will be produced. Together with the solvent phase, the amorphous gel is transferred into an autoclave, which is filled up to

half volumetric capacity as the maximum due to safety considerations stemming from pressure build-up. Next, the autoclave can be sealed and heated up to the temperature configured on the synthesis oven. The solvent phase that is heated up in the autoclave generates the autogenous pressure which facilitates crystallization. Once the crystallization has concluded, the zeolite product can be recovered from the synthesis solution by means of filtration or centrifugation. To better grasp the setup of the autoclave used for hydrothermal synthesis, a depiction of it is available in Figure 2.1.



Figure 2.1: Setup of autoclave for the hydrothermal method¹⁵⁰.

2.3 Powder X-Ray Diffraction

Powder x-ray diffraction (PXRD) is an entrenched technique for determining the structure and phase purity of crystalline solid materials. The technique delivers unique diffraction patterns from crystalline phases, which can then be employed for phase identification (phase ID) of zeolites and countless crystalline solids¹⁵¹. By comparing diffraction patterns of samples with standard patterns, it is possible to identify a zeolite phase and its purity. Should the diffraction pattern exhibit additional unexpected peaks, this alludes to the existence of impurities in the product manifesting a phase of their own.

When a monochromatic x-ray beam comes into contact with a crystalline sample in powder form, x-ray reflections are generated which, depending on the angle of reflection, exhibit greater intensity in comparison to others. By carrying out a spatially-resolved recording of the reflections, an x-ray diffraction pattern can be generated with the generated data. This phenomenon can be explained by the manner in which x-rays interact after being reflected by a set of reiterating lattice planes.

Based on the fundamental principles of x-ray diffraction, which are depicted in Figure 2.2, an x-ray impacting a lattice plane with angle θ will be reflected from the same plane with identical angle. In addition, a further incident x-ray reflecting off a neighbouring plane can affect the first x-ray. Trigonometry demonstrates that the additional distance traversed by the second x-ray is equivalent to $2d \sin(\theta)$, whereby *d* represents the interplanar spacing. In order to observe a diffraction peak, both x-ray photons must be in phase, resulting in constructive interference. The phenomenon only takes place when the traversed distance difference between the two waves is identical to a multiple of the wavelength:

$$n \times \lambda = 2d \times \sin(\theta) \tag{2.1}$$

This correlation is described by Bragg's law in Equation 2.1, which includes the x-ray wavelength, the observed positions of diffraction peaks, and the interplanar spacing from the lattice structure as decisive factors. To obtain data at a single wavelength, a detector scanning a range of angles or a two-dimensional detector can be employed. Alternatively, a wavelength-discriminating detector at a specific angle can be used under white-beam radiation or Bremsstrahlung¹⁵².

In powder diffraction, it is assumed that each particle in the sample possesses a random orientation, leading to the situation that the incident beam comes into contact with the diffraction planes under random angles. Because of the resulting inhomogeneity, sample spinning is utilised to enhance the statistics of data collection. Diverse sample features can affect powder diffraction patterns. For example, a crystallite not larger than 1 µm will lead to broader

diffraction peaks. This is owing to the fact that the decreased amount of planes will add less intensity to any possible reflection from a random particle¹⁵³.



Figure 2.2: Depiction of fundamental principles of x-ray diffraction¹⁵⁴.

For the phase identification of all samples in the project, the capillary powder x-ray diffraction technique was employed. Powder x-ray diffraction patterns were recorded via a STOE STADI-P diffractometer with a Cu-K_{a1} target (wavelength $\lambda = 1.5406$ Å). Furthermore, samples were introduced into borosilicate glass capillaries and spun during measurements, with powder patterns being recorded in the 2 θ diffraction angle range of 5 to 50°. Before filling the capillaries with the samples, the latter were dried overnight at 110°C and then ground into fine powder. Diffraction pattern collection was then carried out at room temperature.

The *Bruker EVA* software was used to establish phase ID. An input file was then created via the program *jEdit* with the *xy*-file of the diffractogram and loaded onto the crystallography program *Topas* for further analysis through Pawley refinement¹⁵⁵. Polynomial fitting of the background to the pattern was employed in the program. Results obtained in the output file are the calculated values for the cell parameters, the goodness of fit and the integral breadth based volume weighted column height (LVoI-IB) as a reference crystallite size. The accuracy of these values depends on the phase purity and crystallinity of the samples. The goodness of fit, which quantifies the discrepancy between the observed diffraction pattern and the expected values under the refined

crystallographic model, is also contemplated for this reason. Any amorphous phase is treated as background, meaning that the goodness of fit applies to the crystalline component. Experimental diffractograms and reference powder patterns from *IZA-SC* for the relevant zeolite framework types have been illustrated using *OriginPro*®¹².

2.4 Electron Microscopy Techniques

2.4.1 Scanning Electron Microscopy

Through scanning electron microscopy, the shape, size and surface properties of synthesised zeolites can be established. To determine the crystal morphologies of the sample, secondary electrons emitted in the scanning electron microscope are generally analysed^{156,157}. These low energy electrons are produced a few nanometres from the surface of the studied material. As a result, the crystallite morphology has a considerable impact on the contrast in the secondary electron imaging¹⁵⁸.

In a standard SEM instrument, a pointed cathode that acts as an electron gun is heated to irradiate electrons¹⁵⁹. These produced electrons are then accelerated through two electrodes, with one being an anode. Afterwards, the accelerated electrons traverse a condenser system, the specimen and an array of magnetic lens in the given order. The purpose of the condenser is to bundle and focus the electrons on a small area of the surface of the specimen. In the case of the magnetic lens, these collect, magnify and relay the signals from the sample to a detector. Figure 2.3 portrays the fundamental measurement principle of SEM.



Figure 2.3: Portrayal of measurement principle of SEM¹⁶⁰.

Regarding the specimen preparation for SEM analysis, a small portion of double-sided carbon tape was cut out and stuck onto the surface of a standard SEM sample stub. Some grains of the finely ground sample were then spread on the exposed side of the carbon tape. This was followed by coating of the sample grains with a thin layer of carbon/gold under a high vacuum environment in order to improve electrical conductivity and promote charge dissipation during analysis. SEM imaging was performed on a JEOL JSM-6700F field emission scanning electron microscope under an operating voltage of 10 kV with a working distance of approximately 8 mm. Images were collected at diverse sites on the surface of the sample under different magnifications.

2.4.2 Energy-Dispersive X-ray Spectroscopy

In conjunction with SEM, energy-dispersive x-ray spectroscopy (EDS) is an analytical technique that can be employed to establish the elemental composition of the studied sample. A specimen inside an electron microscope is bombarded by high-energy electrons, which in turn provokes the excitation and ejection of core-level electrons from the elements present in the investigated material. This is succeeded by a joint relaxation of higher-energy electrons and release of surplus energy in the form of x-ray photons. Because the photons manifest specific energies related to a given element, it is possible to draw a correlation with characteristic transitions belonging to certain elements. As a result, the elemental composition of the sample can be established quantitatively via assessment of these photons. When EDS is carried out in conjunction with SEM, the region of the specimen subjected to the electron beam can be restricted. Measurement of the composition of a defined sample area is thus feasible, which in turn enables tracing of composition shifts across the surface of the sample. On balance, EDS is a very valuable tool for structural analysis and for determining certain sample properties.

2.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is an analytical method by which the elemental oxidation state and composition of a sample can be identified and quantified. One should note that the evolved results and interpretation are restricted to atoms residing very close to the surface of the crystals. The working principle of the technique, illustrated in Figure 2.4, involves irradiation of the surface of the specimen with x-rays of a defined wavelength, thus bringing about electron or photon emission. This phenomenon is called the photoelectric effect. Since the emitted photons or electrons manifest discrete kinetic energies, these can be assigned to the corresponding element and oxidation state. The unique electron shell configuration inside the atom of each element is what enables the distinction between elements¹⁶¹. With the energy of

the x-ray source being maintained at a constant value, the difference between the input energy and the kinetic energy of emitted electrons delivers the value of the energy absorbed by the surface atoms of the studied sample. The absorbed energy, which is defined in Equation 2.2, is known as the binding energy and helps establish the available element and its current oxidation state when contrasted with reference data. Comparison of the intensity between two peaks in a spectrum allows the identification of the relative elemental composition.

$$BE = h \times v - KE \tag{2.2}$$

Binding energy values are plotted as a function of core level photoemission intensity against a broad binding energy range. BE stands for the binding energy, whilst $h \times v$ represents the energy from the x-ray source. In the case of KE, it means the kinetic energy of the emitted electrons which are detected following exposure with the incident x-rays.



Figure 2.4: Schematic depiction of a standard XPS setup, including examples of XP spectra from four different metals as a function of core level photoemission intensity against the binding energy with element specific distribution¹⁶².

Because XPS is a surface sensitive technique, collection of data is restricted to a depth of about 20 nm from the sample surface. In conjunction with an electron beam that sputters down through the specimen for a preestablished distance or time, the bulk of the studied material can be probed via intermittent scans of the newly exposed surface. As the focus of the beam traverses from the surface to the bulk of the sample, it becomes possible to map shifts in elemental composition and oxidation state. For this reason, XPS presents itself as a very beneficial technique in the way it helps establish variations in elemental structure that in turn reflect the functional properties of the material.

2.6 Ultraviolet-Visible Spectroscopy

UV-Vis spectroscopy is an analytical technique which was employed to identify the coordination state of copper in silicoaluminophosphate zeolites that were subjected to ion exchange with Cu²⁺. With this method, it is possible to differentiate between octahedral Cu surrounded by oxygen in CuO particles, and Cu species interacting with the Brønsted acid sites in the zeolite framework¹⁶³. For the measurements, a Perkin Elmer Lambda 950 UV-Vis spectrometer was used under diffuse reflectance mode with an integrating sphere as reflectance probe. Samples were prepared by spreading a thin layer of the studied material in powder form on a section of sellotape which was large enough to cover the back aperture of the integrating sphere cell. UV-Vis absorbance spectra were recorded in the wavelength range from 200 nm to 800 nm.

2.7 Infrared Spectroscopy

Infrared spectroscopy is another analytical technique with extensive use in zeolite characterisation. The method allows for the identification of many zeolite characteristics, such as framework and structure features, silicon to aluminium ratio (Si/AI) ratio, hydroxyl groups, acidity and zeolite-adsorbate interaction. Measurements of radiation absorption lie in the mid-infrared region of the electromagnetic spectrum when employing standard infrared spectrometers, specifically 4000 cm⁻¹ to 400 cm⁻¹ in range¹⁴⁹. Protons which are part of bridging hydroxyl groups in the zeolite framework determine the degree of zeolite acidity. With the assistance of infrared spectroscopy, hydroxyl groups in protonated zeolites can be assessed to obtain qualitative information about the acidity of zeolite samples¹⁴⁹. By introducing probe molecules such as pyridine or ammonia, the acidity can be quantified using the FTIR method. Despite it being possible to attain information about zeolite formation, surface properties, framework vibrations, adsorption and catalysis via FTIR, the technique was mainly utilised in this project for the qualitative assessment of functional groups and zeolite acidity¹⁵⁸.

Zeolite samples in powder form were pressed into circular pellets that could comfortably fit into the KBr window of the spectrometer cell and were thin enough to record a transmission spectrum. To prepare the pellets, approximately 7 mg of each ground sample was placed in a hydraulic press and subjected to a pressure of about 1.2 t. The obtained pellet was fitted into the sample holder and then thermally treated in situ from room temperature to 600°C in 100°C steps. The purpose of the thermal treatment is to eliminate adsorbed water found in the zeolite due to the fact that water exhibits intense adsorption bands in the same region as bridging hydroxyl groups. For each heating step, a transmission spectrum was generated spanning 4000 cm⁻¹ to 400 cm⁻¹ following 64 scans. After the measurement at 600°C, one more transmission spectrum was recorded after cooling down the sample pellet to 50°C. As can be gathered from the literature absorbance spectrum in Figure 2.5, information about the acidity can be inferred from the intense bands around 3627 and 3600 cm⁻¹. These bands may be assigned to the stretching mode of bridging hydroxyl groups, namely the Brønsted OH groups. Furthermore, weak bands at 3745 and 3678 cm⁻¹ imply the existence of P-OH or Si-OH species present on the external surface of the studied zeolite¹⁶⁴.



Figure 2.5: FTIR absorbance spectra of H/SAPO-34 and Cu/SAPO-34 samples after thermal treatment at 500°C¹⁶⁴.

2.8 Solid-state Nuclear Magnetic Resonance Spectroscopy

Solid-state NMR presents itself as an alternative to the more prevalent liquid-state NMR technique when analysing solid materials such as crystals or powders where there is no averaging of anisotropic interactions from Brownian motion. Like in liquid-state NMR, atoms featuring an odd number of neutrons and/or protons manifest a nonzero nuclear spin, leading to degenerate spin states that have equal energy. When an external magnetic field is exerted onto an atom with nonzero nuclear spin, an interaction takes place between the external magnetic field and the nuclear magnetic moment of the atom. This brings about a rift of the degenerate spin states, resulting in unique energy levels. Energy from electromagnetic radiation which is identical to the difference between the two spin states of an atom nucleus leads to resonant absorption. Due to the characteristic magnetic environments from the nuclei in a molecule, it is possible to deduce chemical bonding information and the coordination environment from energy values which exhibit resonant absorption.
Nevertheless, anisotropic interactions with solid systems produce line broadening on the spectra and low-resolution peaks. This effect on the spin behaviour is because of the orientation dependence of nuclei in a molecule and the spatial proximity of their chemical bonds. To solve the problem of the anisotropic effect on solid systems and obtain high-resolution spectra as well as sharp peaks, 'magic angle spinning' (MAS) is employed. In other words, the sample is rotated at an angle of about 54.7° with respect to the direction of the external magnetic field¹⁵⁸. The three main interactions, namely dipolar, chemical shift anisotropy and quadrupolar interactions, are averaged via MAS and their orientation dependency is counteracted.

In this research project, ¹H, ²⁷Al, ²⁹Si and ³¹P MAS NMR spectra of zeolites were collected by utilising a Bruker Avance 300 spectrometer with a widebore 7 T magnet at ambient probe temperature. NMR measurements were performed by Dr Abil Aliev. NMR spectra were further analysed with the help of the programs *Bruker TopSpin®* and *OriginPro®*. The existence of bridging hydroxyls in Si-OH-Al groups (Brønsted acid sites) in the zeolite framework could be established with ¹H MAS NMR spectra. With the assistance of ²⁷Al MAS NMR spectra, it was possible to confirm whether tetrahedrally coordinated Al atoms are available. In addition, the environment of the SiO₄ tetrahedra in the framework was analysed with ²⁹Si MAS NMR spectra. Finally, the presence of tetrahedrally coordinated P atoms could be determined with ³¹P MAS NMR spectra.

Chapter 3: Impact of SAPO-34 Synthesis Parameters on Structural Properties, and Comparison with Small/Medium Pore Zeolites

3.1 Chapter Overview

In this chapter, SAPO-34 synthesis methods and its gel chemistry were explored to improve directed incorporation of silicon into the zeolite framework as well as achieve greater stability. This class of zeolite material was synthesised under hydrothermal conditions using TEAOH as template. The effect of variation of Si-species, its molar ratio in the reactant gel composition, order of addition of reactants, and product recovery methods was studied to evaluate the impact on the yield, phase purity, morphology and the extent of silicon incorporation on framework sites of the products. In addition, samples were subjected to a series of calcination runs at 550, 700 and 900°C to establish how their stability and crystallinity evolve. Via laboratory-based characterisation techniques, it was possible to detect a correlation with the structural properties of SAPO nanoporous systems.

3.2 Introduction

As discussed in chapter one, H-SAPO 34 has shown impressive results as a commercial methanol-to-olefin (MTO) catalyst before Cu-containing CHAtype materials for SCR applications were introduced^{26,27}. However, the fast deactivation and, consequently, brief lifetime arising from coke formation during MTO conversion is one of the main setbacks that affects SAPO-34 catalysts^{29–} ³³. Alternatively, SAPOs with Cu²⁺ cations in extra-framework positions exhibit exceptional activity in SCR of NO with NH₃, which is decisive in tackling pollution brought about by lean burn engines^{34–36}. For this reason, SAPO-34 and -18, as well as other materials exhibiting the CHA and AEI zeolite topology types, are under the spotlight in the field of research for SCR^{37,38}. Even so, problems regarding the hydrothermal stability of Cu-SAPO-34 remain to be solved since the zeolite loses crystallinity and with it also activity under hydrothermal treatment at 900°C³⁹.

As a zeolite which is assigned to the CHA framework type, SAPO-34 mR[Al₁₇P₁₂Si₇O₇₂] (R = diethylamine,morpholine. {e.g. triethylamine, tetraethylammonium hydroxide, etc.) as one possible composition} is a zeotype silicoaluminophosphate that possesses a hexagonal lattice system consisting of two types of composite building units, specifically the d6r (t-hpr) and cha (t-cha) units¹². A depiction of the structure of the CHA framework can be observed in Figure 3.1. Furthermore, it features 3-dimensional interconnected channels with circular 8-ring openings. A broad range of templates can be used to synthesise SAPO-34, for instance TEAOH, TEA, DEA and morpholine^{40–44}. Xu et al. have indicated a laboratory synthetic procedure from Prakash and Unnikrishnan, where the reaction gel of SAPO-34 can be prepared with a molar ratio of Al₂O₃ : 1.06 P₂O₅ : 1.08 SiO₂ : 2.09 R : 66 H₂O (R template. as here morpholine) by using phosphoric acid (85% H₃PO₄), pseudo boehmite (70% Al₂O₃), fumed silica (Degussa Aerosil-200 99+% SiO₂), morpholine (Aldrich, 99% C₄H₉NO), and distilled water^{23,165}. Water that is already present in phosphoric acid and pseudoboehmite should be subtracted from the distilled water which is further added.



Figure 3.1: Illustration of the structure of the CHA framework¹².

The hydrothermal synthetic approach is regarded as the most effective method for synthesising many kinds of zeolites and microporous materials. The effective solvation ability of water, the solubility of the reactants, and the reactivity of the source materials increase in all three cases under hydrothermal synthetic conditions. Consequently, the nucleation and crystallization rate are boosted by promoting the rearrangement and dissolution of the primary gel which is formed in the first stage of synthesis. It is generally assumed that the hydrothermal synthesis process is split in two phases, consisting of the initial formation of the hydrated aluminosilicate gel and the ensuing gel crystallization. Furthermore, it is widely accepted by the scientific community that the crystallization process comprises four steps, these being: (1) condensation of polysilicate and aluminate anions; (2) zeolite nucleation; (3) nuclei growth; and finally (4) crystal growth of zeolites that may lead to secondary nucleation²³. Elucidating the formation mechanism and crystallization process of zeolites continues to be a challenge owing to: a) complex chemical reactions implicated in the whole crystallization process; b) the nucleation and growth of crystals occurring under heterogeneous conditions; and c) the constant fluctuation of the

process²³.

For this reason, the focus is to explore SAPO-34 synthesis methods to improve directed Si incorporation, as well as develop new compositions that exhibit greater stability for potential application in SCR. Connections between synthesis parameters and structural properties were established using laboratory-based characterisation techniques.

3.3 Experimental

Hydrothermal synthesis of SAPO-34 was targeted under variation of parameters, i.e. molar Si-ratios, -precursors in reactant gel and order of addition. The purpose of this is to determine which synthesis conditions deliver products with the most promising properties. For comparison purposes, hydrothermal synthesis of SAPO-57, ZnAPO-57 and silicalite-1 was also performed.

3.3.1 Synthesis

SAPO-34 with Target Gel Composition of 2 mol% Si

For the first stage of hydrothermal synthesis of SAPO-34, a reactant gel composition with the molar ratio $1 \text{ Al} : 0.96 \text{ P} : 0.04 \text{ Si} : 1 \text{ T1} : 30 \text{ H}_2\text{O}$ was targeted under variation of the Si-species, with T1 standing for the template. The following precursors were employed: Al(OH)₃ as Al-species [100 wt%, Sigma-Aldrich], H₃PO₄ as P-species [85 wt% aqueous solution, Sigma-Aldrich], TEAOH as template [40 wt% aqueous solution, Sigma-Aldrich] and water. Four types of Si-species were utilized, these being Ludox® AS-40 colloidal SiO₂ [40 wt% aqueous solution, Sigma-Aldrich], precipitated SiO₂ [100 wt%, Fisher Scientific], tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄) [98 wt%, Sigma-Aldrich] and microspherical SiO₂ (0.5 µm) [100 wt%, Fiber Optic Center].

Regarding the order of precursor addition for the preparation of the reactant gel for hydrothermal synthesis, the selected Si-precursor, water and the TEAOH were mixed together in a PTFE beaker and magnetically stirred at

room temperature for 0.5 h. This was followed by addition of Al(OH)₃ into the above mixture and further magnetic stirring at room temperature for another 0.5 h. Afterwards, H₃PO₄ was poured into the reactant mixture, which was vigorously stirred with a spatula to reduce viscosity of the generated gel, and left for ageing for 0.5 h under magnetic stirring. Finally, 45 ml Teflon-lined steel autoclaves were filled half-way with the produced gel and then placed in a preheated oven for crystallization at 190°C lasting 72 h.

After crystallization, autoclaves were removed and placed in a water bath to cool down to room temperature. The products were then removed from the autoclaves and processes differently. This was achieved by subjecting the product from one autoclave to filtration, whereas the product from another autoclave was left in an ultrasonic bath for an hour, followed by overnight precipitation for separation of solid and liquid phases. For the latter case, both phases were then separated and transferred into two different centrifuge tubes, respectively diluted up to 45 ml with water and centrifuged thrice. All in all, a filter cake and two centrifugates were obtained for each kind of Si-precursor used for the hydrothermal synthesis.

SAPO-34 with Target Gel Composition of 10 and 25 mol% Si

For the second stage of hydrothermal synthesis of SAPO-34, two reactant gel compositions with distinct molar ratios were targeted under variation of the Si-species. These molar ratios were:

- 1 AI: 0.80 P: 0.20 Si: 1 T1: 30 H₂O (10 mol% Si);
- 1 AI: 0.50 P: 0.50 Si: 1 T1: 30 H₂O (25 mol% Si),

with T1 standing for the template. In both cases, the assumption is made that only substitution of P atoms with Si takes place and that no Si islands are formed. This is relevant because the propagation of Si islands is associated with a decrease in Brønsted-acid sites. In reality, Si can pre-nucleate by itself, which in turn facilitates the generation of Si islands.

The following precursors were employed: AI(OH)₃ as AI-species [100 wt%, Sigma-Aldrich], H₃PO₄ as P-species [85 wt% aqueous solution, Sigma-Aldrich], TEAOH as template [40 wt% aqueous solution, Sigma-Aldrich]

and demineralized water. Microspherical SiO₂ (0.5 µm) [100 wt%, Fiber Optic Center] and precipitated SiO₂ [100 wt%, Fisher Scientific] were utilized as Sispecies.

Regarding the order of precursor addition for the preparation of the reactant gel for hydrothermal synthesis, two different approaches were used. These, the crystallization step and product recovery routes are described on Table 3.1. Concerning the order of addition 1, the selected Si-precursor, water and the TEAOH were mixed together in a PTFE beaker and magnetically stirred at room temperature for 0.5 h. This was followed by addition of AI(OH)₃ into the above mixture and further magnetic stirring at room temperature for another 0.5 h. Afterwards, H₃PO₄ was poured into the reactant mixture, which was vigorously stirred with a spatula to reduce viscosity of the generated gel, and left for ageing for 0.5 h under magnetic stirring. With reference to the order of addition 2, H₃PO₄ was first diluted with water in a PTFE beaker and magnetically stirred at room temperature for 0.5 h. Al(OH)₃ was then added to the diluted H₃PO₄ and the formed gel was stirred with a spatula to lower viscosity, followed with more magnetic stirring at room temperature for another 0.5 h. Simultaneously, the Si-precursor was suspended in TEAOH in a separate PTFE beaker and also left to magnetically stir at the same temperature for the same period. Afterwards, the contents of both beakers were poured into a third larger PTFE beaker at the same time and allowed to age under magnetic stirring for 0.5 h. Once the ageing for both orders of addition concluded, 45 ml Teflon-lined steel autoclaves were filled half-way with the produced gels and then placed in a pre-heated oven for crystallization at 190°C lasting 72 h.

Table 3.1: Orders of addition, crystallization method and product recovery steps for hydrothermal synthesis of SAPO-34.

Order of addition 1	Order of addition 2					
1) Si+T1+H ₂ O, + 0.5 h stirring at RT	1) P+H ₂ O, + 0.5 h stirring at RT					
2) Al+{Si+T1+H $_2$ O}, + 0.5 h stirring at RT	2) AI+{P+H ₂ O} / {Si+T}, + 0.5 h stirring at RT					
3) P+{Al+Si+T1+H ₂ O}, + 0.5 h stirring (ageing)	3) {AI+P+H ₂ O}+{Si+T}, 0.5 h stirring (ageing)					
at RT	at RT					
4) Transfer to autoclave for 72 h crystallization at 190°C in pre-heated oven						
5) Product recovery:						
a) Sonification, precipitation with sol. & liq. phase separation, centrifugation ("spc"/"lpc" on						
sample code)						
OR						
b) Filtration ("fc" on sample code)						

After crystallization, autoclaves were removed and placed in a water bath to cool down to room temperature. The products were then removed from the autoclaves and recovered via different routes. This was achieved by subjecting the product from one autoclave to filtration, whereas the product from another autoclave was left in an ultrasonic bath for an hour, followed by overnight precipitation for separation of solid and liquid phases. For the latter case, both phases were then separated and transferred into two different centrifuge tubes, respectively centrifuged thrice and then dried again. Finally, those processing-dependent as-synthesised SAPO-34 samples which exhibit a single crystalline CHA framework with low baseline in XRD patterns were subjected to three series of calcination runs. These were carried out in an air-exposed furnace from room temperature to 550, 700 and 900°C at a rate of 5 K/min, with samples placed in alumina crucibles. Final temperatures were maintained for 10 h, with samples allowed to cool down to room temperature afterwards.

SAPO-57, ZnAPO-57 & Silicalite-1

Because SAPO-57 is a small pore zeolite like SAPO-34, hydrothermal synthesis of SAPO-57 was performed for comparison using the procedure described in a journal article from Broach et al⁶⁹. In contrast to the publication, a reactant gel composition was targeted with the molar ratio given below:

1 AI: 0.50 P: 0.50 Si: 1 T2: 30 H₂O (25 mol% Si),

with T2 standing for the template. The following precursors were employed for SAPO-57: Al(OH)₃ as Al-species [100 wt%, Sigma-Aldrich], H₃PO₄ as P-species [85 wt% aqueous solution, Sigma-Aldrich], microspherical SiO₂ as Si-species (0.5 μ m) [100 wt%, Fiber Optic Center], DEDMAOH as template [20 wt% aqueous solution, Sigma-Aldrich] and deionised water.

The order of precursor addition for the preparation of the reactant gel for the hydrothermal synthesis, the crystallization step and product recovery route are described on Table 3.2. Concerning the order of addition, microspherical SiO₂, water and the template were mixed together in a PTFE beaker and magnetically stirred at room temperature for 0.5 h. This was followed by addition of Al(OH)₃ into the above mixture and further magnetic stirring at room temperature for another 0.5 h. Afterwards, H₃PO₄ was poured into the reactant mixture, which was vigorously stirred with a spatula to reduce viscosity of the generated gel, and left for ageing for 0.5 h under magnetic stirring.

Following ageing, the resultant gel had its pH value lowered to approximately 7.5 via dropwise addition of H₃PO₄ and was then transferred into 45 ml Teflon-lined steel autoclaves. The autoclaves were filled half-way with the produced gel and then placed in a pre-heated oven for crystallization at 175°C for 48 h and 96 h.

Table 3.2: Order of addition, crystallization method and product recovery steps for hydrothermal synthesis of SAPO-57.

Order of addition
1) Si+T1+H ₂ O, + 0.5 h stirring at RT
2) Al+{Si+T1+H ₂ O}, + 0.5 h stirring at RT
3) P+{Al+Si+T1+H ₂ O}, + 0.5 h stirring (ageing) at RT
4) Adjustment of pH to ~7.5 for resultant gel using H_3PO_4
5) Transfer to autoclave for crystallization in pre-heated oven at 175°C for 48 h and 96 h
6) Product recovery via filtration, sonification, decantation, centrifugation

Furthermore, hydrothermal synthesis of SAPO-57 and ZnAPO-57 was performed in accordance with the gel compositions specified in the procedure from the journal article from Broach et al⁶⁹. In the case of ZnAPO-57, which

theoretically possesses a small pore AFV framework like SAPO-57, the synthesis was carried out to observe any differences in the templating effect of the Zn^{2+} cation. Following the publication, the respective reactant gel compositions were targeted with the molar ratio given below:

- 1 AI : 1.25 P : 0.25 Si : 1.56 T2 : 49 H₂O (10 mol% Si);
- 1 AI : 2.4 P : 0.2 Zn : 3.6 T2 : 99 H₂O (5.6 mol% Zn),

with T2 standing for the template DEDMAOH [20 wt% in H₂O, Sigma-Aldrich]. Concerning ZnAPO-57, Broach et al. used a synthesis ratio of (AI + Zn) : P = 1 : 2, even though elemental analysis indicates a ratio of 1 : 1 for the product⁶⁹.

In addition, silicalite-1, which possesses a MFI zeotype framework akin to that of ZSM-5, was also produced via a standard procedure by way of hydrothermal synthesis. The interest behind silicalite-1 lies in the fact that the zeolite manifests hydrophobic behaviour if it is defect free, whereas SAPO-34 possesses a hydrophilic character. Because water entering the pores of SAPO-34 at high temperatures can deteriorate its structure during SCR, it is considered that adding a silicalite-1 shell to it may minimise the impact and improve stability. The correspondent molar ratio of the used reactant gel is:

• 1 Si : 0.14 T3 : 4.92 H₂O,

with T3 standing for the template tetrapropylammonium hydroxide (TPAOH) [1.0 M in H₂O, Sigma-Aldrich]. Pure silicalite-1 can be formed in this manner, however its neutral framework does not allow charge balance for the template.

The following precursors were employed for SAPO-57 and ZnAPO-57: Al(OH)₃ as Al-species [100 wt%, Sigma-Aldrich], H₃PO₄ as P-species [85 wt% aqueous solution, Sigma-Aldrich], DEDMAOH as template and deionised water. In the case of SAPO-57, precipitated SiO₂ [100 wt%, Fisher Scientific] was utilized as Si-species, whereas $Zn(OAc)_2 \cdot 2 H_2O$ [> 99 wt%, Analar] was used for ZnAPO-57. Regarding the synthesis of silicalite-1, the Si-species tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄) [98 wt%, Sigma-Aldrich], the template TPAOH and deionised water were employed.

Regarding the order of precursor addition for the preparation of the reactant gel for hydrothermal synthesis of SAPO-57 and ZnAPO-57, the

82

selected Si/Zn-precursor, water and DEDMAOH were mixed together in a PTFE beaker and magnetically stirred at room temperature for 0.5 h. This was followed by addition of Al(OH)₃ into the above mixture and further magnetic stirring at room temperature for another 0.5 h. Afterwards, H₃PO₄ was poured into the reactant mixture, which was vigorously stirred with a spatula to reduce viscosity of the generated gel, and left for ageing for 0.5 h (SAPO-57) or 1 h (ZnAPO-57) under magnetic stirring. Once the ageing concluded, 45 ml Teflon-lined steel autoclaves were filled half-way with the produced gels and then placed in a pre-heated oven for crystallization at 175°C lasting 72 h (SAPO-57) or 24 h (ZnAPO-57). Concerning the synthesis of silicalite-1 (MFI framework), the Si-precursor, TPAOH and deionised water were blended together in a PTFE beaker and allowed to stir at room temperature for 1 h. A 45 ml Teflon-lined steel autoclave was then filled half-way with the reactant gel, which was allowed to crystallize in a pre-heated oven at 175°C for 24 h.

After crystallization of SAPO-57, ZnAPO-57 and silicalite-1, autoclaves were removed and placed in a water bath to cool down to room temperature. The products were then removed from the autoclaves and recovered via successive routes. To begin with, they were subjected to filtration and then left to dry in an oven at 110°C overnight. Next, the dried products were suspended in water and left to precipitate in an ultrasonic bath for one hour, which was followed by decantation. Finally, the precipitates were transferred into centrifuge tubes, centrifuged thrice and then dried again.

3.3.2 Characterisation

Concerning characterisation, powder X-ray diffraction (PXRD) patterns of samples in borosilicate glass capillaries were recorded using a Stoe system with Cu-K_{a1} radiation (wavelength $\lambda = 1.5406$ Å) in the 2 θ diffraction angle range of 5 to 50°. On the basis of the diffractograms from PXRD, crystallographic properties of the samples were analysed. This was achieved by creating an input file with the *xy*-file of the diffractogram via the program *jEdit* and then loading it to the crystallography program *Topas* for a Pawley refinement with polynomial fitting of the background to the pattern. An output file

83

is then generated with the calculated values for the cell parameters, the goodness of fit and the integral breadth based volume weighted column height as crystallite size. However, these values are more reliable if the samples have a high phase purity and crystallinity, which is why the goodness of fit is also taken into consideration. Any amorphous phase is regarded as background, which means the goodness of fit applies to the crystalline component. For this reason, the obtained diffractograms and the standard powder pattern for the zeolite framework type CHA from *IZA-SC* have been illustrated using *OriginPro*®¹², with the standard powder pattern serving as a suitable reference.

Furthermore, scanning electron microscopy imaging was performed on JEOL JSM-6700F field emission scanning electron microscope under an operating voltage of 10 kV. In conjunction with SEM, elemental mapping spectra from energy-dispersive X-ray spectroscopy (EDS) were obtained using an Oxford Instruments x-act PentaFET Precision detector. In addition, FTIR spectroscopy was performed on a Bruker Alpha FTIR spectrometer to determine the existence of specific functional groups and to conduct a qualitative assessment of zeolite acidity. Approximately 7 mg of each sample were pressed into a thin pellet, fitted into the KBr window of the FTIR in situ cell, and then thermally treated from room temperature to 600°C. Transmission spectra were recorded in steps of 100°C within the range of 4000 to $400 \cdot \text{cm}^{-1}$. Moreover, solid-state nuclear magnetic resonance (NMR) experiments were carried out on Bruker Avance 300 spectrometer with a widebore 7 T magnet at ambient probe temperature. Using a standard Bruker 4 mm double-resonance magic-angle spinning probe with powdered samples packed into zirconia rotors of 4 mm in diameter, ¹H, ²⁷Al, ²⁹Si and ³¹P MAS NMR were recorded respectively at 300.1, 78.2, 59.6 and 121.49 MHz and spun at MAS rates of 12, 12, 8 and 8 kHz with pulse durations of 2, 2, 1 and 0.77 µs, recycle delays of 30, 30, 5 and 120 s, acquisition times of 999.9, 20.4, 42.9 and 44.9 ms, and scans amounting to 8, 511, 29,090 and 12 times. MAS NMR spectra were analyzed via the program Bruker TopSpin®.

84

3.4 Results and Discussion

3.4.1 Powder X-ray Diffraction

SAPO-34 with Target Gel Composition of 2 mol% Si

Together with the used Si-precursors for the hydrothermal syntheses, the calculated cell parameters *a*, *b* and *c*, the goodness of fit, and the LVol-IB crystallite sizes for the samples are listed in Table 3.3. It should be noted that the goodness of fit indicates a better Pawley refinement when its value is closer to 1. The goodness of fit *gof* is defined in Equation 3.1 as the ratio of the reliability factor of the weighted profile r_{wp} and the reliability factor of the expected profile r_{exp} :

$$gof = \frac{r_{\rm wp}}{r_{\rm exp}} \tag{3.1}$$

In addition, the LVol-IB crystallite size gives the reference crystallite size and is determined in the program Topas via the volume-weighted-meancolumn-height method based on integral breadth. Moreover, the estimated errors or standard deviations in this chapter on the refined cell parameters and LVol-IB crystallite size from Topas have been determined for the CHA phase as $a = b = \pm 0.016$ Å, $c = \pm 0.053$ Å, and for the crystallite size as LVol- $IB = \pm 80.364$ nm. Regarding the sample codes for product recovery route, "spc"/"lpc" refer to samples after solid or liquid phase centrifugation, whereas "fc" stands for samples obtained via filtration. On the whole, the values of goodness of fit are highly satisfactory for the samples, with the highest value standing at 3.266. Apart from this, it can be observed that the cell parameters a and b, which lie within the value range of 13.798 Å to 13.807 Å, do not change considerably regardless of the employed Si-precursor. In contrast, cell parameter c exhibits a larger variation from 14.740 Å to 14.805 Å, yet also remains relatively low and does not appear to indicate a trend. Lastly, the LVol-IB crystallite sizes of the SAPO-34 samples derived from Ludox® AS-40

colloidal SiO₂ are generally lower than those of the SAPO-34 samples which were synthesised with other Si-precursors. In the case of the products generated from microspherical SiO₂, the opposite occurs with the LVoI-IB crystallite sizes exceeding almost always those of analogous samples.

Table 3.3: Used Si-precursor, goodness of fit, cell parameters and crystallite size of processing-dependent as-synthesised SAPO-34 samples calculated using Pawley refinement.

Sample Code	Si-Precursor	Goodness of fit [-]	Cell Parameters a, b, c [Å]	LVol-IB crystallite size [nm]
131015[A]_{}_spc		3.266	a = b = 13.798 Å, c = 14.798 Å	59.197
131015[A]_{}_lpc	coll. Ludox AS-40	1.361	a = b = 13.803 Å, c = 14.805 Å	140.60
131015[B]_{}_fc		2.107	a = b = 13.801 Å, c = 14.805 Å	216.42
201015[A]_{}_spc		2.555	a = b = 13.797 Å, c = 14.802 Å	157.83
201015[A]_{}_lpc	prec. SiO ₂	1.681	a = b = 13.807 Å, c = 14.740 Å	150.25
201015[B]_{}_fc		2.297	a = b = 13.800 Å, c = 14.793 Å	306.54
231015[A]_{}_spc		2.548	a = b = 13.803 Å, c = 14.753 Å	234.96
231015[A]_{}_lpc	TEOS	1.450	a = b = 13.805 Å, c = 14.761 Å	127.58
231015[B]_{}_fc		2.212	a = b = 13.806 Å, c = 14.758 Å	4437.6
201115[A]_{}_spc		3.120	a = b = 13.807 Å, c = 14.741 Å	329.67
201115[A]_{}_lpc	microsph. SiO ₂	1.575	a = b = 13.807 Å, c = 14.755 Å	4478.1
201115[B]_{}_fc		2.226	a = b = 13.803 Å, c = 14.774 Å	2270.7

The standard powder pattern for the CHA zeotype framework and the recorded diffractograms for the processing-dependent as-synthesised SAPO-34 samples derived from Ludox® AS-40 colloidal SiO₂ can be observed in Figure 3.2. Major diffraction peaks have been indexed with the Miller indices (*hkl*) from the *IZA-SC* database. When comparing with the standard, 131015[A]_{...}]pc appears to have the best match, as well as a low baseline. 131015[A]_{...}_spc exhibits diffraction peaks which do not appear in the standard diffractogram and must therefore originate from at least another phase in the sample. In addition, it should be pointed out that the baseline, particularly in the angle range from 5 to 30°, is not flat, which may be due to an amorphous component. In the case of 131015[B]_{...}_fc, the diffractogram resembles an averaging out of the other two. The differences resulting from centrifugation or filtration of the products may be due to shifts caused by the recovery route in the particle size distribution of the products and any amorphous content.



Figure 3.2: XRD patterns of CHA standard and three processing-dependent assynthesised SAPO-34 samples derived from Ludox® AS-40 colloidal SiO₂. Normalized intensity is plotted against the diffraction angle 2 θ .

Together with the CHA standard powder pattern, Figure 1 portrays the experimental diffractograms obtained for the processing-dependent assynthesised SAPO-34 samples produced from precipitated SiO₂. Similar to what can be seen in Figure 3.3, sample 201015[A]_{...}_lpc has the lowest baseline and best coincides with the standard diffractogram than the other two experimental recordings. On the other hand, 201015[A]_{...}_spc possesses impurities which can be deduced from the additional diffraction peaks not present in the standard and the elevated baseline. As for 201015[B]_{...}_fc, the recorded diffractogram represents a middle ground between the other experimental patterns.



Figure 3.3: XRD patterns of CHA standard and three processing-dependent assynthesised SAPO-34 samples derived from precipitated SiO₂. Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 3.4 displays the CHA standard powder pattern as well as diffractograms from processing-dependent as-synthesised SAPO-34 samples which feature tetraethyl orthosilicate as their Si-precursor. Following the same trend, the flattest baseline and the most optimal correlation towards the standard powder pattern is exhibited by sample 231015[A]_{...}_lpc. Apart from the main characteristic CHA diffraction peaks, the existence of an amorphous component and presumably other phases can be inferred from further peaks and the uneven baseline in the diffractogram of 231015[A]_{...}_spc. With regard to 231015[B]_{...}_fc, its diffractogram continues the tendency of being an intermediate stage between the other two experimental patterns. All in all, Sisource does not seem to have a meaningful impact on the product outcome regardless of the product recovery route. While the sample patterns match considerably with the CHA standard pattern, for instance at the diffraction peaks (1 0 0) and (-2 1 1), other diffraction peaks, such as the ones near 2 $\theta = 25.2^{\circ}$

and 25.7°, are not identical to the ones from the reference pattern. The relative intensities of these peaks as well as for peak (-1 1 1) also differ between the experimental and standard patterns.



Figure 3.4: XRD patterns of CHA standard and three processing-dependent assynthesised SAPO-34 samples derived from tetraethyl orthosilicate. Normalized intensity is plotted against the diffraction angle 2 θ .

Diffractograms from the CHA standard powder pattern and those from processing-dependent as-synthesised SAPO-34 samples synthesised with microspherical SiO₂ are illustrated in Figure 3.5. Akin to the previous liquid phase centrifugates, 201115[A]_{...}_lpc presents a comparatively smooth baseline and the strongest similarities to the CHA standard pattern. In contrast, a rough baseline and diffraction peaks not corresponding to SAPO-34 are depicted in the diffractogram of 201115[A]_{...}_spc, suggesting one or more extra phases and an amorphous fraction in the sample. In the case of 201115[B]_{...}fc, the diffractogram can be viewed as the result of balancing out the two centrifugate patterns.



Figure 3.5: XRD patterns of CHA standard and three processing-dependent assynthesised SAPO-34 samples derived from microspherical SiO₂. Normalized intensity is plotted against the diffraction angle 2 θ .

SAPO-34 with Target Gel Composition of 10 and 25 mol% Si

Together with the used Si-precursors, -content and order of addition in the hydrothermal syntheses, the calculated cell parameters *a*, *b* and *c*, the goodness of fit, and the LVoI-IB crystallite sizes for the processing-dependent samples are listed in Table 3.4. In addition, a selection of the diffraction patterns after Pawley refinement is available in the Appendices (see Chapter 7.1, Figures 7.1, 7.2 and 7.3). It should be noted that the goodness of fit indicates a better Pawley refinement when its value is closer to 1. Because only some samples exhibit sufficient phase purity and/or crystallinity on their diffraction patterns, the ten which are underlined in the Table are to be discussed. Regarding the sample codes, "spc"/"lpc" refer to samples obtained via filtration. To

begin with, the values of goodness of fit for the underlined samples are quite reasonable, with the values spanning from 1.569 to 2.871. Moreover, it can be observed that the cell parameters *a* and *b*, which lie within the value range of 13.786 Å to 13.792 Å, do not change considerably regardless of the different synthesis parameters. In contrast, cell parameter *c* exhibits a larger variation from 14.872 Å to 14.927 Å, yet also remains relatively low and does not appear to indicate a trend. However, the LVol-IB crystallite size results span a massive area, with results starting as low as 93.515 nm and going as high as 950.90 nm. A pattern cannot be detected which may point out to the cause.

Table 3.4: Used Si-precursor, -content, order of addition, goodness of fit, cell parameters and crystallite size of processing-dependent as-synthesised SAPO-34 samples calculated using Pawley refinement.

Si-	Si-content	Order of	Sample code	Goodness of	Cell parameters a,	LVol-IB crystallite
precursor	[mol%]	addition		fit [-]	b, c [Å]	size [nm]
	10	1	<u>110116[A] {} spc</u>	2.113	<i>a</i> = <i>b</i> = 13.790, <i>c</i> = 14.911	93.515
			110116[A]_{}_lpc	1.189	<i>a</i> = <i>b</i> = 13.800, <i>c</i> = 14.852	43.487
			<u>110116[B] {} fc</u>	2.064	a = b = 13.789, c = 14.912	254.31
		2	<u>120116[A] {} spc</u>	2.421	a = b = 13.792, c = 14.901	950.90
			<u>120116[A] {} lpc</u>	1.716	a = b = 13.792, c = 14.872	372.20
microsph.			<u>120116[B] {} fc</u>	2.133	a = b = 13.790, c = 14.906	278.30
SiO ₂			150116[A]_{}_spc	2.316	a = b = 13.816, c = 14.703	6.2695
		1	150116[A]_{}_lpc	0.875	a = b = 13.741, c = 14.848	3.2474
	25		150116[B]_{}_fc	1.363	a = b = 13.796, c = 14.642	4.9921
		2	180116[A]_{}_spc	1.051	a = b = 13.815, c = 14.480	6.0205
			180116[A]_{}_lpc	0.948	a = b = 13.630, c = 14.454	4.6210
			180116[B]_{}_fc	0.994	a = b = 13.829, c = 14.497	5.1427
	10	1	<u>190116[A] {} spc</u>	2.871	a = b = 13.790, c = 14.927	431.31
			<u>190116[A] {} lpc</u>	2.464	a = b = 13.789, c = 14.927	349.06
			<u>190116[B] {} fc</u>	2.182	a = b = 13.787, c = 14.923	123.81
		2	250116[A] {} spc	1.569	a = b = 13.789, c = 14.902	248.60
			250116[A]_{}_lpc	1.097	a = b = 13.801, c = 14.905	4489.5
prec. SiO ₂			<u>250116[B]_{}_fc</u>	1.799	a = b = 13.786, c = 14.900	296.47
		1	160216[A]_{}_spc	1.186	<i>a</i> = <i>b</i> = 13.801, <i>c</i> = 14.965	4489.5
	25		160216[A]_{}_lpc	0.836	a = b = 13.764, c = 14.822	3.2710
			160216[B]_{}_fc	1.128	a = b = 13.796, c = 14.964	109.44
		2	190216[A]_{}_spc	0.855	a = b = 13.731, c = 14.647	4.1510
			190216[A]_{}_lpc	0.908	a = b = 13.626, c = 14.068	7.3273
			190216[B]_{}_fc	1.012	a = b = 13.901, c = 14.637	5.0086

The standard powder pattern for the CHA zeotype framework and the recorded diffractograms for the processing-dependent as-synthesised SAPO-34 samples derived from microspherical SiO₂ with 10 mol% Si in the reaction gel can be observed in Figure 3.6. Major diffraction peaks have been indexed with the Miller indices (*hkl*) from the *IZA-SC* database. With the exception of 110116[A]_{...}_lpc, the remaining five samples feature excellent overlapping with the standard and also a low baseline. In contrast, 110116[A]_{...}_lpc exhibits characteristic CHA peaks but also a very uneven baseline in comparison to the standard diffractogram, which suggests a high content of amorphous material. In the case of 110116[B]_{...}fc and 120116[B]_{...}_fc, the diffractograms represent a weighted averaging out of their respective "spc" and "lpc" analogues.



Figure 3.6: XRD patterns of a CHA standard and six processing-dependent assynthesised SAPO-34 samples derived from microspherical SiO₂ with 10 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ .

Together with the CHA standard powder pattern, Figure 3.7 portrays the experimental diffractograms obtained for the processing-dependent assynthesised SAPO-34 samples constituted from microspherical SiO₂ with 25 mol% Si in the reaction gel. Unlike to what can be seen in Figure 3.6, none of the samples match with the standard diffractogram. They possess impurities which can be deduced from the additional diffraction peaks; therefore the refined phases of the samples cannot be considered SAPO-34. In the cases of 150116[A]_{...}_spc and 150116[B]_{...}_fc, diffraction peaks belonging possibly to quartz or magadiite appear as well, such as the ones at about $2 \theta = 27.1^{\circ}$ and 27.8° . Furthermore, all the experimental recordings manifest low crystallinity due to the elevated baseline. As for 150116[B]_{...}_fc and 180116[B]_{...}_fc, the recorded diffractograms represent a middle ground between the analogous "spc" and "lpc" experimental patterns.



Figure 3.7: XRD patterns of a CHA standard and six processing-dependent assynthesised SAPO-34 samples derived from microspherical SiO₂ with 25 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 3.8 displays the CHA standard powder pattern as well as diffractograms from processing-dependent as-synthesised SAPO-34 samples which feature precipitated SiO₂ as their Si-precursor with 10 mol% Si in the reaction gel. Except for 250116[A]_{...}_lpc, the other five samples strongly match with the standard and also exhibit a low baseline. Apart from the main characteristic CHA diffraction peaks, samples 250116[A]_{...}_spc and 250116[B]_{...}fc do however show slight impurities because of extra diffraction peaks. As for 250116[A]_{...}_lpc, the existence of an amorphous component and presumably other phases can be inferred from further peaks and the uneven baseline in its diffractogram. With regard to 190116[B]_{...}fc and 250116[B]_{...}fc, their diffractograms continue the tendency of being an intermediate stage between their analogous "spc" and "lpc" experimental patterns.



Figure 3.8: XRD patterns of a CHA standard and six processing-dependent assynthesised SAPO-34 samples derived from precipitated SiO₂ with 10 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ .

Diffractograms from the CHA standard powder pattern and those from processing-dependent as-synthesised SAPO-34 samples synthesised with precipitated SiO₂ at 25 mol% Si in the reaction gel are illustrated in Figure 3.9. Other than 160216[A] {...} spc and 160216[B] {...} fc, the samples do not coincide with the standard diffractogram. Besides this fact, they cannot be contemplated as SAPO-34 due to extra diffraction peaks that indicate impurities. Including 160216[A] {...} spc and 160216[B] {...} fc, the experimental recordings display a high amorphous fraction due to their elevated baseline. With reference to 160216[B]_{...}_fc and 190216[B]_{...}_fc, the diffractograms can be viewed as the result of balancing out their respective centrifugate patterns.



Figure 3.9: XRD patterns of a CHA standard and six processing-dependent assynthesised SAPO-34 samples derived from precipitated SiO₂ with 25 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ .

Calcined SAPO-34 with Target Gel Composition of 10 mol% Si

The PXRD results for the calcined SAPO-34 samples are listed in Table 3.5. Because not all samples exhibit sufficient phase purity and/or crystallinity, the ones which are underlined in the Table are to be discussed. Regarding the sample codes, the tags "c700"/"c900" denote the calcination end temperature at 700 or 900°C. Concerning the values of goodness of fit for the two underlined samples targeting the SAPO-34 framework, these are remarkably close to 1. Furthermore, it can be observed that their cell parameters a and b, which amount to 13.636 Å and 13.644 Å, are not considerably different from one another. Likewise, cell parameter c exhibits little variation at 14.860 Å and 14.855 Å. In previous Tables the cell parameters a and b of SAPO-34 are in the range of approximately 13.75 Å to 13.85 Å, which suggests calcination caused a reduction in the cell parameters. Besides this, the LVol-IB crystallite size strongly diverges, with results standing at 186.52 nm and 127.30 nm. The differentiation between solid and liquid phase centrifugation during product recovery may be the underlying cause behind this discrepancy in the LVol-IB crystallite size.

Table 3.5: Used Si-precursor, -content, order of addition, goodness of fit, cell parameters and crystallite size of calcined SAPO-34 samples calculated using Pawley refinement.

Si-	Si-content	Order of	Sample code	Goodness of	Cell parameters a,	LVol-IB crystallite
precursor	[mol%]	addition		fit [-]	b, c [Å]	size [nm]
microsph. SiO2	10	1	110116[A]_{}_spc/c900	4.874	a = b = 13.620, c = 14.875	7.9093
			110116[B]_{}_fc/c900	4.794	a = b = 13.625, c = 14.854	8.0647
		2	120116[A]_{}_spc/c900	3.627	a = b = 13.618, c = 14.822	201.64
			120116[A]_{}_lpc/c900	5.041	a = b = 13.590, c = 14.728	12.065
			120116[B]_{}_fc/c900	4.000	a = b = 13.617, c = 14.864	8.7887
			<u>190116[A] {}_spc/c900</u>	1.641	<i>a</i> = <i>b</i> = 13.636, <i>c</i> = 14.860	186.52
prec. SiO ₂		1	<u>190116[A] {} lpc/c900</u>	2.337	a = b = 13.644, c = 14.855	127.30
			190116[B]_{}_fc/c900	4.709	a = b = 13.597, c = 14.719	8.2682
		2	250116[A]_{}_spc/c700	0.827	a = b = 13.630, c = 14.820	170.89
			250116[B]_{}_fc/c700	0.887	a = b = 13.631, c = 14.827	136.59

The standard powder pattern for the CHA zeotype framework and the recorded diffractograms for the calcined SAPO-34 samples derived from microspherical SiO₂ with 10 mol% Si in the reaction gel can be observed in Figure 3.10. Major diffraction peaks have been indexed with the Miller indices (*hkl*) from the *IZA-SC* database. The five samples do not overlap strongly with the standard, with extra diffraction peaks appearing around the standard diffraction peak (-2 1 0) that may be from quartz or magadiite. Nevertheless, the baseline on the experimental diffractograms is quite low, suggesting little amorphous material in the samples. In the case of 120116[B]_{...}_fc/c900, the diffractogram represents a weighted averaging out of its respective "spc" and "lpc" analogues.



Figure 3.10: XRD patterns of a CHA standard and five calcined SAPO-34 samples derived from microspherical SiO₂ with 10 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ .

Together with the CHA standard powder pattern, Figure 3.11 portrays the experimental diffractograms obtained for the calcined SAPO-34 samples derived from precipitated SiO₂ as Si-precursor with 10 mol% Si in the reactant gel. Unlike to what can be seen in Figure 3.11, two samples, namely 190116[A] {...} spc/c900 and 190116[A]_{…}_lpc/c900, match with the standard diffractogram quite well. Although 250116[A] {...} spc/c700 and 250116[B] {...} fc/c700 also appear to overlap with the standard pattern, these already show considerable framework deterioration, which is noticeable on the elevated baseline. For this reason, they were not exposed to further calcination at 900°C. With regards to 190116[B] {...} fc/c900, it appears that the SAPO-34 framework has partially disintegrated due to additional peaks near the standard diffraction peak (-2 1 0).



Figure 3.11: XRD patterns of a CHA standard and five calcined SAPO-34 samples derived from precipitated SiO₂ with 10 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ .

SAPO-57, ZnAPO-57, CoAPO-34 & Silicalite-1

Crystallographic properties of SAPO-57, ZnAPO-57, previously assynthesised CoAPO-34 and silicalite-1 samples were analysed in the same manner as the SAPO-34 samples. Furthermore, the *Bruker EVA* software was employed to determine phase ID. The obtained diffractograms and the standard powder patterns for the zeolite framework types LEV, AFV, MFI and CHA from *IZA-SC* have been illustrated using *OriginPro*®¹², with the standard powder patterns serving as suitable references. The calculated cell parameters *a*, *b* and *c*, the goodness of fit, and the LVoI-IB crystallite sizes for the above-mentioned samples are listed in Table 3.6. Moreover, the targeted and actual zeotype phase & class are also available. To begin with, the values of goodness of fit are considerably low for the samples, with the highest value standing at 2.602 for silicalite-1. Concerning the SAPO-57 (10 mol% Si) and ZnAPO-57 samples, these target an AFV framework. It can be observed that they differ considerably in cell parameter *c*, which amounts respectively to 22.762 Å and 12.809 Å. Besides this, the LVol-IB crystallite sizes lie in extreme contrast to one another, with values standing respectively at 913.33 nm and 69.872 nm. Due to this discrepancy, it was found out that the SAPO-57 (10 mol% Si) sample actually has an LEV framework. With regard to the ZnAPO-57 sample, the framework has been established to be AFV, even though the *CIF* file of the standard AFV pattern from *IZA-SC* incorrectly contradicts this. In the case of CoAPO-34 and silicalite-1, they feature respectively a CHA and MFI framework. Because they exhibit distinct phases, their cell parameters and LVol-IB crystallite sizes cannot be compared with one another.

Concerning the three samples targeting the SAPO-57 framework, it can be observed that the cell parameters *a* and *b*, which range from 13.275 Å and 13.283 Å, are not considerably different from one another. Likewise, cell parameter *c* exhibits negligible variation for the SAPO-57 samples at 22.738 Å to 22.762 Å. In contrast, the LVol-IB crystallite size strongly diverges, with results for SAPO-57 samples standing at 913.33 nm and 4489.5 nm. The difference in the molar ratio of Si in the target gel composition may point to the cause.

Table 3.6:	Targe	ted and ac	ctual z	zeot	ype phase	& class,	goo	dness of	fit,	cell
parameters	and	crystallite	size	of	SAPO-57,	ZnAPO-	57,	CoAPO-	34	and
silicalite-1 c	alcula	ted using F	Pawley	ref.	inement.					

Sample code	Targeted zeotype	Targeted/actual zeotype	Goodness of	Cell parameters a, b,	LVol-IB crystallite
	class(es)	phase(s)	fit [-]	c [Å]	size [nm]
120816[A]_{} (10 mol% Si, 72 h)	SAPO-57	AFV/LEV	1.558	a = b = 13.283, c = 22.762	913.33
230516[A]_{} (25 mol% Si, 48 h)	SAPO-57	AFV/LEV	1.125	a = b = 13.275, c = 22.738	4489.5
230516[B]_{} (25 mol% Si, 96 h)	SAPO-57	AFV/LEV	1.115	a = b = 13.279, c = 22.747	4489.5
070916[A]_{}	ZnAPO-57	AFV/AFV	1.502	a = b = 13.393, c = 12.809	69.872
CoAPO-34, pH 7.5, 2h, 150C	CoAPO-34	CHA/CHA	1.082	a = b = 13.781, c = 14.793	39.859
170816_{}_sol	Silicalite-1	MFI/MFI	2.602	a = 19.994, b = 19.832, c = 13.374	90.984

The standard powder pattern for the LEV, AFV, CHA and MFI zeotype frameworks, as well as the recorded diffractograms for samples targeting

SAPO-57 (10 mol% Si), ZnAPO-57, CoAPO-34 and silicalite-1 can be observed in Figure 3.12. Major diffraction peaks have been indexed with the Miller indices (*hkl*) from the *IZA-SC* database. Even though the synthesis of an AFV framework was aimed for in the case of 120816[A]_{...} and 070916[A]_{...}, this was only achieved with the latter. 120816[A]_{...} features an LEV framework when compared with the corresponding standard pattern, e.g. (1 1 2). Regarding 070916[A]_{...}, it does possess an AFV framework despite the AFV reference from *IZA-SC* indicating otherwise as a result of a mistaken space group. Although the CoAPO-34 sample exhibits considerable peak broadening, it overlaps satisfactorily with the CHA reference, e.g. (-1 1 0). Synthesis of silicalite-1 proved to be successful, since its diffraction peaks correlate quite well with those from the MFI reference, e.g. (1 0 1).



Figure 3.12: XRD patterns of LEV, AFV, CHA, and MFI standards, and samples targeting SAPO-57 (10 mol% Si), ZnAPO-57, CoAPO-34 and silicalite-1. Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 3.13 displays the AFV and LEV standard powder patterns as well

as diffractograms from as-synthesised SAPO-57 samples which feature 25 mol% Si in the reactant gel. Even though SAPO-57 was targeted, none of the experimental patterns exhibit any match with the AFV standard pattern. The absence of (0 1 2), (2 0 2) and (2 2 0) for 230516[A]_{...} and 230516[B]_{...}, with respective crystallization times of 48 h and 96 h, is striking. On the other hand, both experimental patterns present agreeable overlapping with the LEV standard pattern. Using the *Bruker EVA* software for phase ID, it appears that SAPO-35 was actually synthesised instead.



Figure 3.13: XRD patterns of AFV and LEV standards and two as-synthesised SAPO-57 samples derived from microspherical SiO₂ with 25 mol% Si in reaction gel. Normalized intensity is plotted against the diffraction angle 2 θ .

3.4.2 Scanning Electron Microscopy and Energy-Dispersive Xray Spectroscopy

SAPO-34 with Target Gel Composition of 10 mol% Si

SEM images were recorded on non-calcined as-synthesised samples 110116[A] {...} spc (10 mol% Si, microspherical SiO₂ as Si precursor, order of addition 1) and 120116[A]_{...}_spc (10 mol% Si, microspherical SiO₂ as Si precursor, order of addition 2) at resolutions of 1 and 10 µm. A selection of these is illustrated in Figure 3.14. Both as-synthesised SAPO-34 samples exhibit cubic-like rhombohedral morphologies²³. In the case of 110116[A] {...} spc, its crystals can be observed in images [a], [b] and [c] being between 8 and 14 µm in length. Furthermore, it is possible to see clumps of presumably amorphous silica which have settled on the SAPO-34 crystals. As for 120116[A] {...} spc, its crystals are portrayed in images [d], [e] and [f]. These have dimensions which range from about 19 to 30 µm. In the same manner as the previous sample, it appears that particles of amorphous silica have agglomerated onto the SAPO-34 crystals.



Figure 3.14: SEM images of $110116[A]_{...}$ spc (10 mol% Si, microspherical SiO₂ as Si precursor, order of addition 1) [a,b,c] and $120116[A]_{...}$ spc (10 mol% Si, microspherical SiO₂ as Si precursor, order of addition 2) [d,e,f].

Furthermore, EDS spectra coupled with SEM images were recorded on the calcined SAPO-34 samples 190116[A]_{...}_spc/c900 and

190116[A]_{...}_lpc/c900 (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor) at a resolution of 100 µm. A selection of these is illustrated in Figure 3.15. Elemental mapping was carried out on SAPO-34 crystals at the tagged points in the SEM images next to the labels "Spectrum 3" [a] and "Spectrum 2" [c]. In image [b], the EDS spectrum of 190116[A]_{...}_spc/c900 can be observed with characteristic signals of O, AI, Si and P standing respectively at about 0.52, 1.49, 1.74 and 2.01 keV. The same applies for 190116[A]_{...}_lpc/c900 in image [d], although in this case there is an additional signal from C at approximately 0.28 keV resulting from the adhesive carbon tab onto which the sample particles rest.

[a]





[c]





Figure 3.15: EDS spectra coupled with SEM images of SAPO-34 samples $190116[A]_{\ldots}$ _spc/c900 [a,b] and $190116[A]_{\ldots}$ _lpc/c900 [c,d] (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor).

3.4.3 Solid-state Nuclear Magnetic Resonance Spectroscopy

Calcined SAPO-34 with Target Gel Composition of 10 mol% Si

Solid-state ¹H, ²⁷Al, ²⁹Si and ³¹P MAS NMR spectra were recorded for the SAPO-34 samples 190116[A]_{...}_spc/c900 and 190116[A]_{...}_lpc/c900 (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor). Their ¹H MAS NMR spectra can be observed in Figure 3.16. Bridging hydroxyls in Si-OH-Al groups (Brønsted acid sites) are inferred by the presence of signals in both spectra respectively at 4.12 and 3.94 ppm¹⁶⁶. However, signal broadening suggests that these sites are hydrated.


Figure 3.16: ¹H MAS NMR spectra of SAPO-34 samples 190116[A] $\{\dots\}$ spc/c900 [top] and 190116[A] $\{\dots\}$ lpc/c900 [bottom] (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor).

Figure 3.17 portrays ²⁷AI MAS NMR spectra of the above samples. The resonance with chemical shifts at 35.39 and 37.65 ppm results from the existence of tetrahedrally coordinated AI atoms in the products^{165,167}.



Figure 3.17: ${}^{27}AI$ MAS NMR spectra of SAPO-34 samples 190116[A] {...} spc/c900 [top] and 190116[A] {...} lpc/c900 [bottom] (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor).

The ²⁹Si MAS NMR spectra with deconvolution results of the SAPO-34 samples 190116[A]_{...}_spc/c900 and 190116[A]_{...}_lpc/c900 (both

10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor) are available in Figure 3.18. The corresponding peaks which describe the environment of the SiO₄ tetrahedra in the framework of 190116[A]_{...}_spc/c900, namely Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al), can be found respectively at -89.97, -94.08, -99.57, -108.55 and -113.66 ppm and possess relative areas which amount to 44.55%, 18.04%, 6.48%, 15.38% and 15.55%¹⁶⁸. In the case of 190116[A]_{...}_lpc/c900, the respective chemical shifts lie at -90, -94.12, -99.86, -108.16 and -113.5, and feature relative areas of 38.26%, 15.2%, 13.16%, 25.46% and 7.91%. Nevertheless, it should be pointed that the chemical shift of these signals is displaced by about 2 to 3 ppm towards the low field due to hydration.



Figure 3.18: ²⁹Si MAS NMR spectra with deconvolution results of SAPO-34 samples 190116[A]_{...}_spc/c900 [top] and 190116[A]_{...}_lpc/c900 [bottom] (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor).

Finally, the ³¹P MAS NMR spectra of the aforementioned samples are illustrated in Figure 3.19. Here, tetrahedrally coordinated P atoms in the framework can be deduced from the strong peaks at -28.47 and -28.57 ppm¹⁶⁹.



Figure 3.19: ³¹P MAS NMR spectra of SAPO-34 samples 190116[A] $\{\dots\}$ spc/c900 [top] and 190116[A] $\{\dots\}$ lpc/c900 [bottom] (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor).

3.4.4 Infrared Spectroscopy

FTIR Spectroscopy of Commercial SAPO-34

FTIR spectra of commercial SAPO-34, which are illustrated in Figure 3.20, were recorded at different temperatures to observe Brønsted acid sites and specific functional groups related to the framework, as well as to have a reference on this class of material. IR bands located at distinct wavelength regions act as unique identifiers which allow a qualitative assessment of zeolite acidity and the recognition of these functional groups. To begin with, the IR band in the region around 3588 · cm⁻¹ is indicative of the existence of bridging Si-OH-AI groups. However, it appears concealed at room temperature due to moisture and becomes more distinct with increasing temperatures as a result of dehydration¹⁷⁰. This situation reverts after the sample pellet is cooled down to 50°C. Furthermore, the band at 1642 · cm⁻¹ at room temperature proves that there is adsorbed water at first, which gradually vanishes with the *in situ* thermal treatment⁴¹. Regarding the functional groups of the SAPO-34 framework, the IR band at around 490 · cm⁻¹ reveals the presence of T-O bends originating from SiO₄ and AlO₄ framework tetrahedra. The band located in the region of 630 · cm⁻¹ points to the existence of D6R rings, which are a distinctive CHA composite building unit⁷². In addition, symmetric stretching of P-O or Al-O groups are inferred from the reduced transmittance at approximately $720 \cdot \text{cm}^{-1}$. Lastly, the band at around 1099 cm⁻¹ can be assigned to asymmetric stretching of O-P-O groups⁷².



Figure 3.20: Transmittance FTIR spectra of commercial SAPO-34 at different temperatures.

FTIR Spectroscopy of Calcined SAPO-34 with Target Gel Composition of 10 mol% Si

ATR-FTIR spectra of the SAPO-34 samples 190116[A]_{...}_spc/c900 and 190116[A]_{...}_lpc/c900 (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor) were recorded at room temperature to analyse and identify specific functional groups in the compounds. Together with manually picked peaks, Figure 3.21 displays the transmittance IR spectra of the samples. The IR band at around $413 \cdot \text{cm}^{-1}$ points to the existence of T-O bends originating from SiO₄ and AlO₄ framework tetrahedra. This also applies to D6R rings, a distinctive CHA composite building unit, which can be inferred from the band located at around $630 \cdot \text{cm}^{-1}$. In addition, symmetric stretching of P-O or Al-O groups can be concluded from the reduced transmittance at approximately $670 \cdot \text{cm}^{-1}$. At around $1075 \cdot \text{cm}^{-1}$, asymmetric stretching of O-P-O groups is observable. Apart from this, the band at $1634 \cdot \text{cm}^{-1}$ indicates the presence of adsorbed water⁴¹. Lastly, existence of hydroxyl Si-OH-Al groups cannot be proved because their characteristic band at about 3434 · cm⁻¹ is absent as a consequence of hydration.



Figure 3.21: Transmittance ATR-FTIR spectra of SAPO-34 samples 190116[A]_{...}_spc/c900 [blue] and 190116[A]_{...}_lpc/c900 [red] (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si-precursor).

3.5 Conclusions and Discussion

Judging from the XRD patterns of the SAPO-34 samples with a target gel composition of 2 mol% Si, it can be concluded that the liquid phase centrifugates deliver the greatest phase purity and a higher relative crystallinity due to the low baseline. Furthermore, most SAPO-34 samples produced from a reaction gel with 10 mol% Si display high crystallinity in the recorded diffractograms and match quite well with the CHA standard powder pattern. On the other hand, those obtained from 25 mol% Si in the reaction gel exhibit an elevated content of amorphous material and thus feature an uneven baseline.

With regard to the remaining XRD patterns, it can be concluded that the synthesis of ZnAPO-57 delivered an AFV framework while following the literature procedure of Broach et al. However, this was not the case of SAPO-57, which in turn exhibited an LEV framework. In the case of the previously as-synthesised CoAPO-34, this sample appears to match with the CHA reference in spite of peak broadening. Furthermore, the pattern of silicalite-1 appears to correlate satisfactorily with the pattern of the MFI reference, meaning that the synthesis was effective.

After subjecting processing-dependent as-synthesised SAPO-34 samples to calcination runs, it has been determined that 190116[A] {...} spc/c900 and 190116[A] {...} lpc/c900 are the only samples to maintain relatively intact their CHA framework. Both are derived from precipitated SiO₂ with 10 mol% Si in the reaction gel, following the order of addition 1 during synthesis. Regarding the solid-state MAS NMR spectra, the samples 190116[A] {...} spc/c900 and 190116[A] {...} lpc/c900 (both 10 mol% Si in reactant gel, precipitated SiO₂ as Si precursor) possess the characteristic signals of SAPO-34. Nevertheless, the signal broadening in the ¹H MAS NMR spectra and the slight displacement of the correspondent peaks for Si(4AI), Si(3AI), Si(2AI), Si(1AI) and Si(0AI) from their standard chemical shift in the ²⁹Si MAS NMR spectra suggests that the samples are hydrated. In addition to SEM revealing the cubic-like rhombohedral morphology of the SAPO-34 crystals, EDS spectra also confirm the existence of Si, Al, P and O, implying that silicoaluminophosphates are at hand. Finally, the FTIR spectra of commercial and as-synthesised SAPO-34 show bands originating from T-O bends, D6R rings, symmetric stretching of P-O or AI-O groups and asymmetric stretching of O-P-O groups. In the case of hydroxyl Si-OH-Al groups, these are at first not observable because of hydration. The respective IR band only reveals itself after the in situ thermal treatment of SAPO-34. For this reason, the presence of adsorbed water further justifies the abovementioned interpretation of the ¹H and ²⁹Si MAS NMR spectra.

Chapter 4: Investigation of Synthesis Methods for Silicalite-1@SAPO-34 Structures and Contrast with Analogous Zeolite Blends

4.1 Chapter Overview

In this chapter, shell@core synthesis variations for silicalite-1@SAPO-34 compositions were investigated to understand the underlying gel chemistry and improve the stability of these structures. The main concern of study is how the crystallinity, structural properties and stability are affected by changing synthesis parameters. To tackle these issues, modification of the surface structure of SAPO-34 has been proposed through the growth of a continuous hydrophobic silicalite-1 shell over SAPO-34 core crystals which protects the core from water during SCR while still maintaining the desired properties. To prepare these shell@core compositions, SAPO-34 was employed as seed crystal in silicalite-1 reactant gels under different synthesis parameters and proportions. Furthermore, pre-treatment of core crystals was performed via ion exchange with TPABr or hydrolysis condensation of SiO₂ with TEOS onto them prior to synthesis of shell@core systems. Laboratory-based characterisation techniques were employed to understand how the gel chemistry impacts upon shell@core type nanoporous systems.

4.2 Introduction

Zeolitic molecular sieves, which play a crucial role in catalytic and separation processes, exhibit uniform three-dimensional nano-channels with characteristic distribution and strength of acid sites⁷¹. External crystal surfaces, internal channels with differing acid strengths and shape sieving behaviors affect the nature of chemical reactions⁷². Even though zeolitic molecular sieves possess an insignificant concentration of external surface active sites, they still have a considerable impact in catalytic reactions because they impose

118

diffusional restrictions on reactants that flow into active sites in micropores⁷³. There have been efforts to enhance the selectivity properties and reactivity of zeolites by altering their external surface area⁷². Functionalization of the external surface of zeolites has been carried out by means of steaming, acid leaching, element surface modification, etc. in order to obtain mesopores and a suitable acid distribution⁷⁷. However, employing the forecited techniques brings about partial damage and species deposition, which in turn may lead to a decrease in the effective diameter of pore openings and thus a drop in catalytic activity. To obtain the sought-after catalytic properties, the growth of a continuous shell over core crystals has been proposed as an alternative for customizing the surface structure⁷². Under these circumstances, a shell that is responsible for the functionality and stability of the composite also sets the limits for access to a core with different features⁷⁸.

With the help of two distinct sequential crystallization procedures which rely on the shell and core materials, Razavian and Fatemi have described the synthesis of ZSM-5/SAPO-34 binary nanostructured composites⁷². A strategy has been proposed to protect SAPO-34 crystals in the strong basic precursor media of ZSM-5 where the novel bi-phase SAPO-34/ZSM-5 (core/shell) zeolite composite is formed⁷². Despite the fact that SAPO-34 and ZSM-5 share neither chemical compatibilities nor similar framework compositions, the stability of SAPO-34 in a harsh synthesis media was safeguarded by pre-treating the zeolite. A hierarchical composite can be created with tuned surface properties and adjusted distribution of active centres by merging useful physicochemical characteristics of these two types of zeolites, namely CHA and MFI⁷². The adsorptive, sieving and catalytic functions that accompany both zeotype structures are combined and compiled according to wish, making these materials useful in more application fields.

SAPO-34 possesses hydrophilic character. Its framework can be damaged and deactivated when exposed to moisture and temperatures above 650°C¹²¹. On the other hand, silicalite-1, if defect free, manifests hydrophobic behaviour. It is therefore considered that adding a hydrophobic silicalite-1 shell to SAPO-34 may screen the core from contact with water, minimise the impact of water at high temperatures and improve stability. For this reason, the focus is to create stable shell@core structures from SAPO-34 (core) and silicalite-1

119

(shell) and thus identify the most successful synthesis pathways. Connections between synthesis parameters and structural properties as well as stability were established using laboratory-based characterisation techniques.

4.3 Experimental

Hydrothermal synthesis of silicalite-1@SAPO-34 materials was targeted under variation of parameters, i.e. core crystal mass per reactant gel volume, crystallization time and pre-treatment of core crystals. The goal is to establish which synthesis conditions deliver shell@core systems with optimal features. In addition, mechanical mixtures of silicalite-1 and SAPO-34 were prepared with different weight ratios to compare analysis results with those of attempted silicalite-1@SAPO-34 materials.

4.3.1 Synthesis

Synthesis of Silicalite-1@SAPO-34/CoAPO-34 as a Function of Seed Crystal Mass per Reactant Gel Volume

The first stage of hydrothermal synthesis of shell@core materials which was attempted consisted of silicalite-1@CoAPO-34 and silicalite-1@SAPO-34. For this purpose, previously as-synthesised CoAPO-34 (CHA framework) and SAPO-34 seed crystals from the samples 190116[A]_{...}_spc/c900 and 190116[A]_{...}_lpc/c900 were utilized as core material and introduced into silicalite-1 reactant gels under variation of seed crystal mass per gel volume. In the case of CoAPO-34, it is a blue compound that was taken as a reference for colour contrast purposes. The employed synthesis and crystallization procedure for these shell@core materials was the same as with silicalite-1. With the exception of one shell@core material synthesis in a 45 ml Teflon-lined steel autoclave, these were carried out in 21 ml Teflon-lined steel autoclaves. Table 4.1 summarizes the synthesis plan for the shell@core materials of silicalite-1@CoAPO-34 and silicalite-1@SAPO-34 as a function of seed crystal mass per gel volume.

Table 4.1: Performed synthesis plan of shell@core materials of silicalite-1@CoAPO-34 and silicalite-1@SAPO-34 as a function of seed crystal mass per silicalite-1 gel volume.

Targeted shell@core	Sample code	Targeted mass of seed	Gel volume
composite		crystal for core [g]	[ml]
	150916_{}_comp,sol	0.4	10.5
Silicalite-1@CoAPO-34	190916_{}_comp,sol	0.2	10.5
	200916_{}_comp,sol	0.1	10.5
	160816_{}_comp,sol	0.5	22.5
Silicalite-1@SAPO-34	220916_{}_comp,sol	0.4	10.5
	270916_{}_comp,sol	0.6	10.5
	280916_{}_comp,sol	0.8	10.5

After crystallization, autoclaves were removed and placed in a water bath to cool down to room temperature. All products were then removed from the autoclaves and recovered via successive routes. To begin with, they were subjected to filtration and then left to dry in an oven at 110°C overnight. Next, the dried products were suspended in water and left to precipitate in an ultrasonic bath for one hour, which was followed by decantation. Finally, the precipitates were transferred into centrifuge tubes, centrifuged thrice and then dried again.

Synthesis of Silicalite-1@SAPO-34 as a Function of Crystallization Time and TPABr Pre-Treatment with Pre-Crystallization

The second stage of hydrothermal synthesis of shell@core materials consisting of silicalite-1@SAPO-34 was attempted to establish if the surface hydrophobicity of SAPO-34 can be controlled by generating a silicalite-1 shell. Firstly, the following molar ratio was used to prepare the silicalite-1 reactant gel in a PTFE beaker under magnetic stirring at room temperature:

• 1 Si : 0.14 T1 : 4.92 H₂O,

with the Si-species tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄) [98 wt%, Sigma-Aldrich], the template TPAOH [1.0 M in H₂O, Sigma-Aldrich] (T1) and deionised water being employed as precursors.

Two approaches were taken to attempt the hydrothermal synthesis of the shell@core materials. For the first approach, calcined as-synthesised SAPO-34 seed crystals were utilized as core material and introduced into the reactant gel at a ratio of 0.4 g of SAPO-34 per 10.5 ml of silicalite-1 gel. In a PTFE beaker, the blend was allowed to magnetically stir at room temperature for 1 h. 21 ml Teflon-lined steel autoclaves were then filled half-way with the reactant mixture, which was allowed to crystallize in a pre-heated oven at 175°C for 48 h, 72 h, 96 h and 120 h.

Following a procedure from Razavian and Fatemi, the second approach involved first subjecting SAPO-34 to two ion exchanges with TPABr [98 wt%, Aldrich⁷². 3 g of SAPO-34 were allowed to stir at room temperature for 2 h in a 60 ml 2-propanol [≥ 99.5 wt%, Emplura] solution of 1 M TPABr. Afterwards, the ion exchanged compound was filtered, washed with deionised water, allowed to dry in an oven, and then subjected to a second ion exchange by repeating the same procedure. Next, a silicalite-1 reactant gel was prepared using the above molar ratio, stirred at room temperature for 1 h, and then transferred into 45 ml Teflon-lined steel autoclaves for pre-crystallization at 170°C for 8 h. After cooling down the pre-crystallization slurry in a water bath, it was then mixed with the double ion exchanged SAPO-34 in a PTFE beaker at a ratio of 0.4 g of seed crystal per 10.5 ml of silicalite-1 slurry and left stirring at room temperature for 1 h. 21 ml Teflon-lined steel autoclaves were then filled half-way with the resultant mixture, which was allowed to crystallize in a pre-heated oven at 170°C for 3 h, 5 h, 7 h and 9 h. Table 4.2 summarizes the synthesis plan for the silicalite-1@SAPO-34 materials as a function of crystallization time and whether SAPO-34 was pre-treated via ion exchange.

Table 4.2: Performed synthesis plan of silicalite-1@SAPO-34 materials as a function of crystallization time and pre-treatment of SAPO-34 core via ion exchange.

Sample code	Ion exchange of SAPO-34?	Crystallization time [h]
071216[A]_{}_s@c,sol		48
121216[A]_{}_s@c,sol	No	72
121216[B]_{}_s@c,sol		96
071216[B]_{}_s@c,sol		120
190117[A]_{}_s@c,sol		3
190117[B]_{}_s@c,sol	Yes	5
190117[C]_{}_s@c,sol		7
190117[D]_{}_s@c,sol		9

After crystallization, autoclaves were placed in a water bath to cool down to room temperature. All products were then removed from the autoclaves and recovered via slightly different routes. In the case of the products without ion exchanged SAPO-34, these were subjected to filtration and then left to dry in an oven at 110°C overnight. Next, these dried products and those with ion exchanged SAPO-34 were suspended in water and left to precipitate in an ultrasonic bath for one hour, which was followed by decantation. After this, the precipitates were transferred into centrifuge tubes, centrifuged thrice and then dried again. Finally, those attempted as-synthesised shell@core samples which exhibit both crystalline CHA and MFI frameworks with a relatively low baseline in XRD patterns were subjected to calcination. This was carried out in an airexposed furnace from room temperature to 550°C at a rate of 5 K/min, with samples placed in alumina crucibles. The final temperature was maintained for 10 h, with samples allowed to cool down to room temperature afterwards.

Synthesis of Silicalite-1@SAPO-34 as a Function of Crystallization Time and TPABr Pre-Treatment without Pre-Crystallization

The third stage of hydrothermal synthesis of shell@core materials consisting of silicalite-1@SAPO-34 was carried out to establish whether a silicalite-1 shell can be generated without the pre-crystallization step from the second stage. Firstly, the following molar ratio was used to prepare the silicalite-

1 reactant gel in a PTFE beaker under magnetic stirring at room temperature:

• 1 Si : 0.14 T1 : 4.92 H₂O,

with the Si-species tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄) [98 wt%, Sigma-Aldrich], the template TPAOH [1.0 M in H₂O, Sigma-Aldrich] (T1) and deionised water being employed as precursors.

Two approaches were taken to attempt the hydrothermal synthesis of the shell@core materials. For the first approach, seed crystals of commercial SAPO-34 were utilized as core material and introduced into the reactant gel at a ratio of 0.4 g of SAPO-34 per 10.5 ml of silicalite-1 gel. In a PTFE beaker, the blend was allowed to magnetically stir at room temperature for 1 h. 21 ml Teflon-lined steel autoclaves were then filled half-way with the reactant mixture, which was allowed to crystallize in a pre-heated oven at 170°C for 24 h, 48 h, 72 h and 96 h.

The second approach involved repeating the procedure of Razavian and Fatemi with 4 g of SAPO-34 in a 75 ml 2-propanol solution of 1 M TPABr, with the difference being that drying was carried out at room temperature⁷². After performing the second ion exchange and preparing the silicalite-1 reactant gel, 0.4 g of the double ion exchanged SAPO-34 were added per 10.5 ml of reactant gel and the blend was allowed to stir at room temperature for 1 h. The resultant mixture was then filled half-way into 21 ml Teflon-lined steel autoclaves. This was followed by crystallization in a pre-heated oven at 170°C for 3 h, 5 h, 7 h, 9 h, 24 h, 48 h, 72 h and 144 h. For the purpose of PXRD comparison, a separate silicalite-1 reactant gel with the same molar ratio but without SAPO-34 was left stirring at room temperature for 24 hours in order to let water evaporate and form a dry silicalite-1 gel, which was further dried in an oven at 110°C overnight. Besides this, silicalite-1 was synthesised by utilizing the mentioned molar ratio. The precursors were blended together in a PTFE beaker and allowed to stir at room temperature for 1 h. This was followed by crystallization in 21 ml Teflon-lined steel autoclaves at 170°C for 2 h, 6 h and 24 h. Table 4.3 summarizes the synthesis plan for the silicalite-1@SAPO-34 materials as a function of crystallization time and whether SAPO-34 was pre-treated via ion exchange; it also includes the double ion exchanged SAPO-34 and the dry silicalite-1 gel.

Table 4.3: Performed synthesis plan of silicalite-1@SAPO-34 materials as a function of crystallization time and pre-treatment of SAPO-34 core via ion exchange; double ion exchanged SAPO-34, dry silicalite-1 gel and silicalite-1 are also listed.

Sample code	Ion exchange of SAPO-34?	Crystallization time [h]
260417_{SAPO-34}_2ie(TPABr)	Yes	_
[Double ion exchanged SAPO-34]	103	
160517_{}_gel [Dry silicalite-1 gel]	-	-
060717[A]_{}_sol [Silicalite-1(2h)]	-	2
060717[B]_{}_sol [Silicalite-1(6h)]	-	6
060717[C]_{}_sol [Silicalite-1(24h)]	-	24
030417[A]_{}_s@c,sol [Silicalite-1@SAPO-34(24h)]		24
030417[B]_{}_s@c,sol [Silicalite-1@SAPO-34(48h)]	No	48
030417[C]_{}_s@c,sol [Silicalite-1@SAPO-34(72h)]		72
030417[D]_{}_s@c,sol [Silicalite-1@SAPO-34(96h)]		96
310517[A]_{}_s@c,sol [Silicalite-1@2ieSAPO-34(3h)]		3
310517[B]_{}_s@c,sol [Silicalite-1@2ieSAPO-34(5h)]		5
310517[C]_{}_s@c,sol [Silicalite-1@2ieSAPO-34(7h)]		7
310517[D]_{}_s@c,sol [Silicalite-1@2ieSAPO-34(9h)]	Ves	9
020517[A]_{}_s@c,sol [Silicalite-1@2ieSAPO-34(24h)]		24
020517[B]_{}_s@c,sol [Silicalite-1@2ieSAPO-34(48h)]		48
020517[C]_{}_s@c,sol [Silicalite-1@2ieSAPO-34(72h)]]	72
020517[D]_{}s@c,sol [Silicalite-1@2ieSAPO-34(144h)]		144

After crystallization, autoclaves were placed in a water bath to cool down to room temperature and the products were removed from the autoclaves. All crystallization products were then suspended in water and left to precipitate in an ultrasonic bath for one hour, which was followed by decantation. After this, the precipitates were transferred into centrifuge tubes, centrifuged thrice and then dried in an oven at 110°C overnight.

Preparation of Mechanical Mixtures of SAPO-34 with Silicalite-1, Synthesis of Silicalite-1 at Different pH Values, and Synthesis of Silicalite-1@SAPO-34 as a Function of Crystallization Time and Hydrolysis Condensation

In the fourth stage, ten mechanical mixtures of commercial SAPO-34 with as-synthesised silicalite-1 were prepared with different weight ratios to compare analysis results with those of attempted silicalite-1@SAPO-34 materials. These are specified in Table 4.4.

Table 4.4: Mechanical mixtures of commercial SAPO-34 with as-synthesised silicalite-1 according to employed weight ratios.

Sample code	Weight ratio of SAPO-34/Silicalite-1 [-]	Weight ratio of Silicalite-1/SAPO-34 [-]
0.06 SAPO-34 : 1.0 Silicalite-1	0.06	
0.21 SAPO-34 : 1.0 Silicalite-1	0.21	
0.36 SAPO-34 : 1.0 Silicalite-1	0.36	1.0
0.51 SAPO-34 : 1.0 Silicalite-1	0.51	
0.66 SAPO-34 : 1.0 Silicalite-1	0.66	
0.06 Silicalite-1 : 1.0 SAPO-34	0.06	
0.21 Silicalite-1 : 1.0 SAPO-34	0.21	
0.36 Silicalite-1 : 1.0 SAPO-34	0.36	1.0
0.51 Silicalite-1 : 1.0 SAPO-34	0.51	
0.66 Silicalite-1 : 1.0 SAPO-34	0.66	

In addition, hydrothermal synthesis of silicalite-1 was carried out at different pH values to verify its feasibility. The following molar ratio was used to prepare the silicalite-1 reactant gel in a PTFE beaker under magnetic stirring at room temperature:

• 1 Si : 0.14 T1 : 4.92 H₂O,

with the Si-species tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄) [98 wt%, Sigma-Aldrich], the template TPAOH [1.0 M in H₂O, Sigma-Aldrich] (T1) and deionised water being employed as precursors. Besides this, phosphoric acid (H₃PO₄) [85 wt% aqueous solution, Sigma-Aldrich] was also added dropwise to attain the different values; these pH values were 7.05, 8.25, 9.53 and 10.59, whereas the pH value of the silicalite-1 reactant gel without H₃PO₄ lies between 11.5 and 12.

Concerning the synthesis of silicalite-1, the Si-precursor, TPAOH and deionised water were blended together in a PTFE beaker and allowed to stir at room temperature for 1 h. Afterwards, the resultant gel was spread evenly in four Teflon beakers, and their pH values were adjusted to the abovementioned values by dropwise addition of H₃PO₄. Four 21 ml Teflon-lined steel autoclaves were then filled half-way with each reactant gel and crystallized in a pre-heated oven at 170°C for 24 h.

Furthermore, an alternative strategy for the hydrothermal synthesis of silicalite-1@SAPO-34 via hydrolysis condensation was employed. Two approaches were taken to attempt the hydrothermal synthesis of these

shell@core materials. For the first approach, 3 g of seed crystals of SAPO-34 from a commercial supplier were utilized as core material (ratio of 1 g of SAPO-34 per 10.5 ml of final reactant gel) and suspended in a solution of 30 ml deionised water and 60 ml 2-propanol [≥ 99.5 wt%, Emplura], and allowed to stir at room temperature for 10 min; this was followed by the slow addition of 18 g TEOS and further stirring for 10 min. The reactant mixture was then split evenly among three Teflon beakers. Whilst stirring, 0.3 ml acetic acid (CH₃CO₂H) [96 wt%, Acros Organics] was added in the first beaker, whereas 0.34 ml ammonia solution (NH₃) [28 wt% aqueous solution, Analar NORMAPUR] was included in the second beaker (bearing in mind a target concentration of ~0.5 M in the deionised water for both cases); nothing was further given to the third beaker, and the contents of the three beakers were left stirring for 3 h. Then, the product slurries were transferred into centrifuge tubes, centrifuged four times and then dried in an oven at 110°C overnight. After drying, the centrifugates were placed in three separate Teflon beakers and diluted with a solution of 14.42 g deionised water and 23.08 g TPAOH (1.0 M) based on the molar ratio of the silicalite-1 reactant gel, which was divided equally amongst the three beakers; the reactant mixtures were left stirring at room temperature for 1 h. 21 ml Teflon-lined steel autoclaves were then filled half-way with the resultant gels, which were allowed to crystallize in a pre-heated oven at 170°C for 24 h.

For the second approach, hydrolysis condensation of TEOS with acetic acid was employed as an intermediary step for the hydrothermal synthesis of silicalite-1@SAPO-34 and silicalite-1 samples. The following molar ratio was used for the hydrolysis condensation reaction of TEOS:

• 1 TEOS : 1 AcOH : 4 H₂O.

Here, 18 g TEOS was added in each of two Teflon beakers, with 3 g of commercial SAPO-34 being suspended in one beaker (ratio of 1 g of SAPO-34 per 10.5 ml of final reactant gel) for the preparation of silicalite-1@SAPO-34 and allowed to stir at room temperature for 10 min.; whilst stirring, this was followed by the dropwise addition of 21.19 g acetic acid (96 wt%) diluted with 4.89 g deionised water in each beaker and further stirring for 20 min. Next, the product slurries were transferred into centrifuge tubes, centrifuged four times and then dried in an oven at 110°C overnight. After drying, the centrifugates were placed in two separate Teflon beakers and diluted with a solution of

127

28.85 g deionised water and 46.15 g TPAOH (1.0 M) based on the molar ratio of the silicalite-1 reactant gel, which was divided equally amongst the two beakers; the reactant mixtures were left stirring at room temperature for 1 h. 21 ml Teflon-lined steel autoclaves were then filled half-way with the resultant gels, which were allowed to crystallize in a pre-heated oven at 170°C for 24 h, 48 h and 144 h. Table 4.5 summarizes the synthesis plan for the silicalite-1 and silicalite-1@SAPO-34 materials as a function of synthesis medium factors and crystallization time.

Table 4.5: Performed synthesis plan of silicalite-1 and silicalite-1@SAPO-34 materials as a function of synthesis medium and crystallization time.

Sample code	Synthesis medium	Crystallization time
	factors	[h]
260717[A]_{}_sol [Silicalite-1(24h/pH7.05)]	pH = 7.05	
260717[B]_{}_sol [Silicalite-1(24h/pH8.25)]	pH = 8.25	24
260717[C]_{}_sol [Silicalite-1(24h/pH9.53)]	pH = 9.53	27
260717[D]_{}_sol [Silicalite-1(24h/pH10.59)]	pH = 10.59	
110817[A]_{}_s@c,sol [Silicalite-1@SAPO-34(24h/iPrOH+AcOH)]	iPrOH + AcOH	
110817[B]_{}_s@c,sol [Silicalite-1@SAPO-34(24h/iPrOH+NH ₃)]	iPrOH + NH ₃	24
110817[C]_{}_s@c,sol [Silicalite-1@SAPO-34(24h/iPrOH)]	iPrOH	
230817[A]_{}_s@c,sol [Silicalite-1@SAPO-34(24h/AcOH)]	AcOH	24
230817[B]_{}_s@c,sol [Silicalite-1@SAPO-34(48h/AcOH)]	AcOH	48
230817[C]_{}_s@c,sol [Silicalite-1@SAPO-34(144h/AcOH)]	AcOH	144
230817[D]_{}_sol [Silicalite-1(24h/AcOH)]	AcOH	24
230817[E]_{}_sol [Silicalite-1(48h/AcOH)]	AcOH	48
230817[F]_{}_sol [Silicalite-1(144h/AcOH)]	AcOH	144

After crystallization, autoclaves were placed in a water bath to cool down to room temperature and the products were removed from the autoclaves. All crystallization products were then suspended in water and left to precipitate in an ultrasonic bath for one hour, which was followed by decantation. After this, the precipitates were transferred into centrifuge tubes, centrifuged thrice and then dried in an oven at 110°C overnight. Finally, those attempted assynthesised silicalite-1@SAPO-34 samples derived from hydrolysis condensation of TEOS with acetic acid were subjected to calcination. This was carried out in an air-exposed furnace from room temperature to 550°C at a rate of 5 K/min, with samples placed in alumina crucibles. The final temperature was maintained for 10 h, with samples allowed to cool down to room temperature

afterwards.

Cu(II) Ion Exchange of SAPO-34 and of Silicalite-1@SAPO-34 derived from Hydrolysis Condensation

In the fifth stage, Cu(II) ion exchange was carried out on commercial SAPO-34 and on three previous silicalite-1@SAPO-34 samples derived from hydrolysis condensation of TEOS with acetic acid to determine if systems containing SAPO-34 with Cu²⁺ cations in extra-framework positions can be generated like those found in literature which possess exceptional activity in NH₃-SCR, with the difference here being the presence of a hydrophobic silicalite-1 shell. First of all, 0.3 g of each of the four samples were subjected to ion exchange in a 30 ml aqueous solution of 0.01 M copper(II) acetate monohydrate (Cu(OAc)₂ · H₂O) [99 wt%, Fluka] at 50°C for one hour under stirring. The resulting ion-exchanged samples were then transferred into centrifuge tubes, centrifuged thrice and allowed to dry in an oven at 110°C for one hour. Finally, the four compounds were subjected to calcination. This was carried out in an air-exposed furnace from room temperature to 550°C at a rate of 5 K/min, with samples placed in alumina crucibles. The final temperature was maintained for 10 h, with products allowed to cool down to room temperature afterwards. The samples which were subjected to Cu(II) ion exchange are listed in Table 4.6.

Table 4.6: Sample list for Cu(II) ion exchange involving commercial SAPO-34 and three samples targeting silicalite-1@SAPO-34 materials derived from hydrolysis condensation following 24 h, 48 h and 144 h crystallization.

Sample code
SAPO-34(com.)_ie(Cu)/c550 [Cu/SAPO-34(c550)]
230817[A]_{}_s@c,sol/ie(Cu)/c550 [Silicalite-1@Cu/SAPO-34(24h/AcOH/c550)]
230817[B]_{}_s@c,sol/ie(Cu)/c550 [Silicalite-1@Cu/SAPO-34(48h/AcOH/c550)]
230817[C]_{}_s@c,sol/ie(Cu)/c550 [Silicalite-1@Cu/SAPO-34(144h/AcOH/c550)]

4.3.2 Characterisation

Regarding characterisation, powder X-ray diffraction (PXRD) patterns of samples in borosilicate glass capillaries were recorded using a Stoe system with Cu-K_{a1} radiation (wavelength $\lambda = 1.5406$ Å) in the 2 θ diffraction angle range of 5 to 50°. On the basis of the diffractograms from PXRD, crystallographic properties of the samples were analyzed. To begin with, the Bruker EVA software was used to establish phase ID. An input file with the xyfile of the diffractogram was then created via the program *jEdit* and loaded to the crystallography program *Topas* for a Pawley refinement with polynomial fitting of the background to the pattern. An output file is then generated with the calculated values for the cell parameters, the goodness of fit and the integral breadth based volume weighted column height as crystallite size. However, these values are more reliable if the samples have a high phase purity and crystallinity, which is why the goodness of fit is also taken into consideration. Any amorphous phase is regarded as background, which means the goodness of fit applies to the crystalline component. The obtained diffractograms and the standard powder patterns for the zeolite framework types MFI and CHA from IZA-SC have been illustrated using OriginPro®¹², with the standard powder patterns serving as suitable references.

In addition, scanning electron microscopy imaging was performed on JEOL JSM-6700F field emission scanning electron microscope under an operating voltage of 10 kV. In conjunction with SEM, elemental mapping spectra from energy-dispersive X-ray spectroscopy (EDS) were obtained using an Oxford Instruments x-act PentaFET Precision detector. Besides this, X-ray photoelectron spectroscopy was performed for composition analysis by using a Thermo Scientific K α instrument with a monochromated AI K α X-ray source at 1486.6 eV that was operated in constant analyzer energy (CAE) mode. High resolution and survey spectra were recorded with a respective pass energy of 50 and 200 eV, and a respective binding energy step size of 0.1 and 1.0 eV. Scans were carried out at a spot size of 400 µm. XPS spectra were analyzed via the programs *Thermo Avantage*® and *CasaXPS*®. Finally, UV-Vis spectra were recorded with the help of a Perkin Elmer Lambda 950 UV-Vis

130

spectrometer. Samples were analysed in powder form on sellotape within an integrating sphere chamber.

4.4 Results and Discussion

4.4.1 Powder X-ray Diffraction

Synthesis of Silicalite-1@SAPO-34/CoAPO-34 as a Function of Seed Crystal Mass per Reactant Gel Volume

To begin with, the calculated cell parameters a, b and c, the goodness of fit, and the LVol-IB crystallite sizes for the silicalite-1@CoAPO-34 and silicalite-1@SAPO-34 samples are listed in Table 4.7. Besides this, the targeted and actual zeotype phase, class, and seed crystal mass per gel volume in the hydrothermal syntheses are also available. Furthermore, the estimated errors or standard deviations in this chapter on the refined cell parameters and LVol-IB crystallite size from Topas have been determined for the CHA phase as $a = b = \pm 0.042$ Å, $c = \pm 0.081$ Å, for the MFI phase as $a = \pm 0.174$ Å, $b = \pm 0.225$ Å, $c = \pm 0.124$ Å, and for the crystallite size LVolas $IB = \pm 114.76$ nm. Because not all samples exhibit sufficient phase purity and/or crystallinity, the two samples which are underlined in the Table are to be discussed. Given the fact that the underlined shell@core materials have the lowest and highest seed crystal mass (or amount of sites) per gel volume in their silicalite-1@SAPO-34 synthesis series, it is possible that this has an effect on their more pronounced crystallinity. In the case of the silicalite-1@CoAPO-34 series, the inferior crystallinity of the core may be responsible for the formation of essentially amorphous compounds. The values of goodness of fit, which is a measure of the quality of the Pawley refinement, lie in the proximity of 1 for the underlined samples and are thus highly satisfactory. In addition, these materials share similar cell parameters for both the CHA (e.g. a = b = 13.827 and 13.793 Å) and MFI (e.g. c = 13.167 and 13.288 Å) components. On the other hand, the LVol-IB crystallite sizes differ strongly at 459.07 nm and 4489.0 nm, perhaps due to divergent seed crystal masses per gel volume.

Table 4.7: Targeted and actual zeotype phase, class, seed crystal mass per gel volume, goodness of fit, cell parameters and crystallite size of shell@core materials calculated using Pawley refinement.

Sample code	Targeted	Targeted/actual	Seed	Gel	Goodness	Cell parameters	LVol-IB
	zeotype	zeotype phase(s)	crystal	volume	of fit [-]	a, b, c [Å]	crystallite
	class(es)		mass [g]	[ml]			size [nm]
150916_{}_comp,sol	Silicalite- 1@CoAPO-34	CHA & MFI/amorphous	0.4	10.5	0.926	a = b = 13.601, c = 14.790 (CHA); a = 19.956, b = 19.499, c = 13.086 (MFI)	6.2281
190916_{}_comp,sol	Silicalite- 1@CoAPO-34	CHA & MFI/amorphous	0.2	10.5	0.901	a = b = 13.722, c = 15.268 (CHA); a = 20.140, b = 19.646, c = 13.264 (MFI)	10.471
200916_{}_comp,sol	Silicalite- 1@CoAPO-34	CHA & MFI/amorphous	0.1	10.5	1.431	a = b = 13.782, c = 14.983 (CHA); a = 20.012, b = 19.741, c = 13.187 (MFI)	20.354
<u>160816 {} comp,sol</u>	Silicalite- 1@SAPO-34	CHA & MFI/CHA & MFI	0.5 (= 0.23)	22.5 (= 10.5)	1.826	a = b = 13.827, c = 14.957 (CHA); a = 19.994, b = 19.723, c = 13.167 (MFI)	459.07
220916_{}_comp,sol	Silicalite- 1@SAPO-34	CHA & MFI/amorphous	0.4	10.5	1.119	a = b = 13.762, c = 15.173 (CHA); a = 20.185, b = 19.856, c = 13.258 (MFI)	12.499
270916_{}_comp,sol	Silicalite- 1@SAPO-34	CHA & MFI/amorphous	0.6	10.5	1.026	a = b = 13.693, c = 15.076 (CHA); a = 20.349, b = 19.792, c = 13.225 (MFI)	18.051
280916 {} comp.sol	Silicalite- 1@SAPO-34	CHA & MFI/CHA & MFI	0.8	10.5	1.096	a = b = 13.793, c = 14.911 (CHA); a = 19.970, b = 19.778, c = 13.288 (MFI)	4489.0

Together with the CHA and MFI standard powder patterns, Figure 4.1 portrays the experimental diffractograms obtained for three attempted assynthesised shell@core materials consisting of silicalite-1@CoAPO-34. These composites differ in their seed crystal mass per gel volume, with an ascending mass starting from the top pattern. Regardless of the fact that 200916_{...}_comp,sol shows in part the standard peaks of the MFI reference for peaks (1 0 1) and (5 0 1), all three samples are practically amorphous with very elevated baselines on their XRD patterns and indicate a failed attempt in the synthesis of a MFI@CHA material. This may be due to unfavourably high pH values ranging from about 10 to 11.5 before crystallization during the hydrothermal synthesis. However, it remains to be identified whether further lowering the seed crystal mass per gel volume may actually benefit the formation of a shell@core material.



Figure 4.1: XRD patterns of CHA and MFI standards and three attempted assynthesised silicalite-1@CoAPO-34 materials. Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 4.2 displays the CHA and MFI standard powder patterns as well as diffractograms from four targeted as-synthesised shell@core materials based on silicalite-1@SAPO-34. Once again, the seed crystal mass per gel volume is different for each sample, with a descending mass beginning from the top pattern. While 160816_{...}_comp,sol starts off by manifesting a strong match with the MFI reference, e.g. (1 0 1) and (5 0 1), the sample 280916_{...}_comp,sol offers an adequate overlapping with the CHA reference via the peaks (-1 1 0) and (-2 1 0). Even though 220916_{...}_comp,sol and 270916_{...}_comp,sol feature low crystallinity given their high baseline, the former displays a few peaks which link to the MFI standard, while the latter shows a similar behaviour with the CHA standard. This seems to indicate a gradual substitution of the zeolite framework type which is dependent on the seed crystal mass per gel volume. Nevertheless, there is no evident success in the synthesis of a MFI@CHA material, perhaps because of elevated pH values standing between 11 and 11.5 prior to crystallization.



Figure 4.2: XRD patterns of CHA and MFI standards and four attempted assynthesised silicalite-1@SAPO-34 materials. Normalized intensity is plotted against the diffraction angle 2 θ .

Synthesis of Silicalite-1@SAPO-34 as a Function of Crystallization Time and TPABr Pre-Treatment with Pre-Crystallization

The calculated cell parameters a, b and c, the goodness of fit, and the LVol-IB crystallite sizes for commercial SAPO-34 (SAPO-34(com.)) and silicalite-1@SAPO-34 samples are listed in Table 4.8. Moreover, the targeted and actual zeotype phase, class, and crystallization time are also available. Sample codes with the tag "c550" denote the sample has been subjected to calcination at 550°C, whereas the goodness of fit is meant to indicate a better Pawley refinement the closer its value is to 1. Despite SAPO-34(com.) exhibiting a goodness of fit that is somewhat distant of 1, its XRD pattern appears highly crystalline and is that of a CHA framework, and for that reason will also be used as a reference when comparing the patterns of the attempted silicalite-1@SAPO-34 materials. Samples 071216[A] {...} s@c,sol and 071216[B] {...} s@c,sol, which did not undergo ion exchange, are essentially amorphous and therefore lattice parameters cannot be taken into consideration. Nevertheless, 121216[A] {...} s@c,sol and 121216[B] {...} s@c,sol also did not have their SAPO-34 seed crystals pre-treated, and yet they exhibit at least an MFI framework. A continuous trend dependent on the crystallization time is not evident since the amorphous samples occupy both extremes of the performed crystallization times, so a plausible explanation would be a mistake or an impurity during the preparation of the reactant gels. Even so, this synthesis approach did not result in a product with both the CHA and MFI frameworks. Regarding the two samples with MFI frameworks, it can be observed that their cell parameters a, b and c are not considerably different from one another. In contrast, the LVol-IB crystallite size diverges considerably, with results standing at 131.96 nm and 106.37 nm.

As for the samples 190117[A]_{...}_s@c,sol, 190117[A]_{...}_s@c,sol, 190117[A]_{...}_s@c,sol, 190117[A]_{...}_s@c,sol and their calcined homologues, which are products of the second synthesis approach, these clearly feature CHA and MFI diffraction peaks in their XRD patterns. However, this does not necessarily mean that MFI@CHA materials are present, since a mechanical mixture of the corresponding crystals would also display a similar pattern. Concerning the cell parameters of these attempted silicalite-1@SAPO-

135

34 materials, the values before calcination for both the CHA and MFI components are quite similar and only change slightly after calcination, most likely as a result of template removal. Apart from this, the LVoI-IB crystallite sizes remain invariably the same prior to and after calcination.

Table 4.8: Targeted and actual zeotype phase, class, goodness of fit, cell parameters and crystallite size of commercial SAPO-34 and attempted silicalite-1@SAPO-34 materials calculated using Pawley refinement.

Sample code	Crystallization	Targeted	Targeted/actual	Goodness	Cell parameters	LVol-IB
	time [h]	zeotype class(es)	zeotype phase(s)	of fit [-]	a, b, c [A]	crystallite size [nm]
SAPO-34(com.)	-	SAPO-34	CHA/CHA	2.187	<i>a</i> = <i>b</i> = 13.684, <i>c</i> = 14.856	4396.7
071216[A]_{}_s@c,sol	48	Silicalite- 1@SAPO-34	MFI & CHA/amorphous	-	-	-
121216[A]_{}_s@c,sol	72	Silicalite- 1@SAPO-34	MFI & CHA/MFI	1.502	a = 19.972, b = 19.773, c = 13.376 (MFI)	131.96
121216[B]_{}_s@c,sol	96	Silicalite- 1@SAPO-34	MFI & CHA/MFI	1.769	a = 19.960, b = 19.768, c = 13.357 (MFI)	106.37
071216[B]_{}_s@c,sol	120	Silicalite- 1@SAPO-34	MFI & CHA/amorphous	-	-	-
190117[A]_{}_s@c,sol	3	Silicalite- 1@SAPO-34	MFI & CHA/MFI & CHA	1.276	a = b = 13.625, c = 14.798 (CHA); a = 20.003, b = 19.804, c = 13.349 (MFI)	4489.5
190117[B]_{}_s@c,sol	5	Silicalite- 1@SAPO-34	MFI & CHA/MFI & CHA	1.269	a = b = 13.627, c = 14.804 (CHA); a = 19.992, b = 19.759, c = 13.195 (MFI)	4489.5
190117[C]_{}_s@c,sol	7	Silicalite- 1@SAPO-34	MFI & CHA/MFI & CHA	1.456	a = b = 13.627, c = 14.798 (CHA); a = 20.001, b = 19.746, c = 13.304 (MFI)	4489.5
190117[D]_{}_s@c,sol	9	Silicalite- 1@SAPO-34	MFI & CHA/MFI & CHA	1.251	a = b = 13.639, c = 14.802 (CHA); a = 20.011, b = 19.796, c = 13.361 (MFI)	4489.5
190117[A]_{}_s@c,sol/c550	3	Silicalite- 1@SAPO-34	MFI & CHA/MFI & CHA	1.786	a = b = 13.585, c = 14.816 (CHA); a = 20.034, b = 19.832, c = 13.184 (MFI)	4489.5
190117[B]_{}_s@c,sol/c550	5	Silicalite- 1@SAPO-34	MFI & CHA/MFI & CHA	1.345	a = b = 13.591, c = 14.813 (CHA); a = 20.063, b = 19.857, c = 13.306 (MFI)	4489.5
190117[C]_{}_s@c,sol/c550	7	Silicalite- 1@SAPO-34	MFI & CHA/MFI & CHA	1.333	a = b = 13.589, c = 14.815 (CHA); a = 20.033, b = 19.835, c = 13.302 (MFI)	4489.5
190117[D]_{}_s@c,sol/c550	9	Silicalite- 1@SAPO-34	MFI & CHA/MFI & CHA	1.186	a = b = 13.593, c = 14.806 (CHA); a = 20.045, b = 19.844, c = 13.351 (MFI)	4489.5

The standard powder pattern for the CHA and MFI zeotype frameworks, as well as the recorded diffractograms for commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials can be observed in Figure 4.3. Major diffraction peaks have been indexed with the Miller indices (hkl) from the IZA-SC database. The shell@core materials have not been subjected to ion exchange and only differ in their crystallization time, with a descending crystallization time starting from the top pattern. Whereas 071216[A] {...} s@c,sol and 071216[B]_{...}_s@c,sol are practically amorphous with very elevated baselines on their XRD patterns, 121216[A] {...} s@c,sol and 121216[B] {...} s@c,sol match only with the MFI reference, e.g. (1 0 1) and (5 0 1). Even so, this indicates a failed attempt in the synthesis of an MFI@CHA material. None of them overlap with the CHA reference, only the highly crystalline SAPO-34(com.) correlates well with the standard pattern, e.g. (-1 1 0) and (-2 1 0). However, it should be pointed that a trend cannot be detected with regard to the crystallization time. This is because both extremes only result in amorphous products, while 121216[A] {...} s@c,sol and 121216[B] {...} s@c,sol feature at least a zeotype phase. As was mentioned above, the underlying cause may be an error or impurity during the reactant gel preparation.



Figure 4.3: XRD patterns of CHA and MFI standards, commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials (without ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction angle 2 θ .

Together with the CHA and MFI standard powder patterns, Figure 4.4 portrays SAPO-34(com.) and the experimental diffractograms obtained for four attempted as-synthesised silicalite-1@SAPO-34 materials. In contrast to the previous series of shell@core materials, these products have had their SAPO-34 seed crystals pre-treated via ion exchange with TPABr. Apart from this, these materials also experienced different crystallization times, with a descending crystallization time starting from the top pattern. Even though the attempted silicalite-1@SAPO-34 materials do not display a very low baseline and therefore not a very high crystallinity, the peaks corresponding to both MFI and CHA frameworks are readily observable, e.g. (1 0 1) for MFI and (-2 1 0) for CHA. Therefore, this may mean that ion exchange plays a role in protecting the SAPO-34 crystals in the strong basic synthesis media (pH \approx 14). On the other hand, there appears to be no major shift in the intensity of the diffraction peaks

when comparing with the baseline and between zeotype phases. That is in spite of the moderate variation in crystallization time. However, it remains to be seen whether further increasing the crystallization time considerably may actually improve the crystallinity of the final product.



Figure 4.4: XRD patterns of CHA and MFI standards, commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials prior to calcination (with ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 4.5 displays the CHA and MFI standard powder patterns as well as diffractograms from SAPO-34(com.) and the previous four targeted silicalite-1@SAPO-34 materials after calcination at 550°C. As a reminder, the crystallization time differs between shell@core materials, with a descending crystallization time beginning from the top pattern. It can be noticed after calcination that the experimental silicalite-1@SAPO-34 still overlap well with the MFI and standard patterns, e.g. (101) for MFI and (-210) for CHA. Furthermore, the products possess a somewhat low baseline, suggesting reasonable crystallinity. However, one significant change is the reduction observed in the intensity of the CHA peaks on the experimental patterns, especially of 190117[D] {...} s@c, sol/c550, after calcination. This may come as a result of template removal and/or differences in the stability of the zeotype after longer crystallization time. In the phases а case of 190117[D] {...} s@c,sol/c550, the longer crystallization time could be responsible for the stronger drop in intensity of the CHA diffraction peaks. In view of this, increasing the crystallization time as was mentioned earlier may actually lead to a counter-productive loss of crystallinity after calcination.



Figure 4.5: XRD patterns of CHA and MFI standards, commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials after calcination (with ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction angle 2 θ .

Synthesis of Silicalite-1@SAPO-34 as a Function of Crystallization Time and TPABr Pre-Treatment without Pre-Crystallization

Crystallographic properties of double ion exchanged commercial SAPO-34, dry silicalite-1 gel, silicalite-1 and attempted silicalite-1@SAPO-34 samples were analyzed. However, because all silicalite-1@SAPO-34 samples appear to be essentially amorphous in their diffractograms, it was not possible to carry out a Pawley refinement with the crystallography program *Topas*. As a result, there are no respective values of the attempted silicalite-1@SAPO-34 samples for the cell parameters, the goodness of fit and the integral breadth based volume weighted column height as crystallite size. The obtained diffractograms and the standard powder patterns for the zeolite framework types MFI and CHA from *IZA-SC* have been illustrated using *OriginPro®*¹², with the standard powder patterns serving as suitable references.

The targeted and actual zeotype phase, class, and crystallization time for the above-mentioned samples are listed in Table 4.9. Sample codes with the tag "2ie" denote double ion exchanged SAPO-34 has been employed in the synthesis of the sample, whereas the crystallization time is designated between parentheses, e.g. "(24h)". Silicalite-1 samples were produced to follow via their XRD patterns the evolution of the crystallization of their MFI framework over different crystallization times, and for that reason will be used as references along with the dry silicalite-1 gel and double ion exchanged SAPO-34 when comparing with the amorphous patterns of the attempted silicalite-1@SAPO-34 materials. This series of silicalite-1@SAPO-34 samples appear amorphous regardless of the core material being subjected to ion exchange or not. It is understandable in the cases where unmodified SAPO-34 was added in a strong basic synthesis medium (pH \approx 11), leading to the dissolution of its CHA framework. As for the products which included ion exchanged SAPO-34 in the hydrothermal synthesis, a plausible explanation would be a mistake or an impurity during the preparation of the reactant gels. Another possibility lies in the fact that the modified SAPO-34 was dried at room temperature after ion exchange and washing instead of being dried in an oven at an elevated temperature.

Table 4.9: Targeted and actual zeotype phase, class and crystallization time of double ion exchanged commercial SAPO-34, dry silicalite-1 gel, silicalite-1 and attempted silicalite-1@SAPO-34 materials.

Sample code	Crystallization time	Targeted zeotype	Targeted/actual zeotype
	[h]	class(es)	phase(s)
Silicalite-1@SAPO-34(24h)	24	Silicalite-1@SAPO-34	MFI & CHA/amorphous
Silicalite-1@SAPO-34(48h)	48	Silicalite-1@SAPO-34	MFI & CHA/amorphous
Silicalite-1@SAPO-34(72h)	72	Silicalite-1@SAPO-34	MFI & CHA/amorphous
Silicalite-1@SAPO-34(96h)	96	Silicalite-1@SAPO-34	MFI & CHA/amorphous
Silicalite-1@2ieSAPO-34(3h)	3	Silicalite-1@SAPO-34	MFI & CHA/amorphous
Silicalite-1@2ieSAPO-34(5h)	5	Silicalite-1@SAPO-34	MFI & CHA/amorphous
Silicalite-1@2ieSAPO-34(7h)	7	Silicalite-1@SAPO-34	MFI & CHA/amorphous
Silicalite-1@2ieSAPO-34(9h)	9	Silicalite-1@SAPO-34	MFI & CHA/amorphous
Silicalite-1@2ieSAPO-	24	Silicalite-1@SAPO-34	MFI & CHA/amorphous
34(24h)	27	Onicante reorri o or	
Silicalite-1@2ieSAPO-	48	Silicalite-1@SAPO-34	MFI & CHA/amorphous
34(48h)	40		
Silicalite-1@2ieSAPO-	72	Silicalite-1@SAPO-34	MFI & CHA/amorphous
34(72h)	12		
Silicalite-1@2ieSAPO-	144	Silicalite-1@SAPO-34	MFI & CHA/amorphous
34(144h)			
Silicalite-1(2h)	2	Silicalite-1	MFI/MFI
Silicalite-1(6h)	6	Silicalite-1	MFI/MFI
Silicalite-1(24h)	24	Silicalite-1	MFI/MFI
Dry silicalite-1 gel	-	Silicalite-1	MFI/amorphous
Double ion exchanged	_	SAPO-34	СНА/СНА
SAPO-34			

The standard powder pattern for the MFI zeotype framework, as well as the recorded diffractograms for dry silicalite-1 gel and three silicalite-1 samples with different crystallization times can be observed in Figure 4.6. Major diffraction peaks have been indexed with the Miller indices (*hkl*) from the *IZA-SC* database. To begin with, the dry silicalite-1 gel is essentially amorphous. In the case of silicalite-1(2h), crystallization is already stepping in after 2 h, even though the baseline remains somewhat elevated. Despite this, the fraction of amorphous material consistently keeps on dropping with longer crystallization crystallization times, which is inferable on the baselines of silicalite-1(6h) and silicalite-1(24h). All diffraction peaks present in the diffractograms of these silicalite-1 samples correspond to the MFI zeotype framework, e.g. (1 0 1) and (5 0 1).



Figure 4.6: XRD patterns of MFI standard, dry silicalite-1 gel and three silicalite-1 samples with different crystallization times. Normalized intensity is plotted against the diffraction angle 2 θ .

Together with the CHA and MFI standard powder patterns, Figure 4.7 portrays the experimental diffractograms obtained for four attempted assynthesised silicalite-1@SAPO-34 materials. The shell@core materials have not been subjected to ion exchange and only differ in their crystallization time. It can be recognized that all samples consist basically of only amorphous material, and therefore do not match with the MFI and CHA references. The strong basic synthesis medium (pH \approx 11) is likely responsible for the breakup of the CHA zeotype framework of the core material.


Figure 4.7: XRD patterns of CHA and MFI standards and four samples targeting silicalite-1@SAPO-34 materials (without ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 4.8 displays the CHA and MFI standard powder patterns as well as diffractograms from double ion exchanged commercial SAPO-34 and four targeted as-synthesised silicalite-1@SAPO-34 materials. In contrast to the previous series of shell@core materials, the ones here have had their SAPO-34 seed crystals undergo ion exchange. Apart from this, these materials also experienced different crystallization times, which amounted to 3 h, 5 h, 7 h and 9 h. In the same manner as the previous series of shell@core materials, these are practically amorphous and do not overlap in any way with the MFI and CHA standard patterns. By comparison, ion exchanged SAPO-34, which was employed as a precursor, maintains its CHA framework after undergoing ion exchange, e.g. (-1 1 0) and (-2 1 0). Despite the previous surface treatment of commercial SAPO-34 with TPABr, this does not seem to have protected the SAPO-34 crystals from the strong basic synthesis medium (pH \approx 11). As was mentioned earlier, the underlying cause behind the amorphous nature of these

targeted shell@core materials may be an error or impurity during the reactant gel preparation, or the manner in which the modified SAPO-34 was dried after ion exchange.



Figure 4.8: XRD patterns of CHA and MFI standards, double ion exchanged commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials following 3 h, 5 h, 7 h and 9 h crystallization (with ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction angle 2 θ .

The standard powder patterns for the CHA and MFI frameworks, as well as the recorded diffractograms of the double ion exchanged commercial SAPO-34 and four attempted as-synthesised silicalite-1@SAPO-34 materials, are illustrated in Figure 4.9. In the same way as with the previous series, ion exchanged SAPO-34 was added as core material for the hydrothermal synthesis of the shell@core materials. By contrast, the crystallization times have been extended to 24 h, 48 h, 72 h and 144 h. Despite the dramatic increase in crystallization time, all attempted shell@core materials appear completely amorphous and do not correlate whatsoever with the MFI and CHA references, including the crystalline ion exchanged SAPO-34. Once again, surface treatment of the core material does not appear to make its CHA framework more resilient towards the strong basic synthesis medium. The absence of silicalite-1 pre-crystallization, or the drying method of commercial SAPO-34 after subjecting it to ion exchange, may be implicated in the total absence of MFI and CHA frameworks in the attempted shell@core materials.



Figure 4.9: XRD patterns of CHA and MFI standards, double ion exchanged commercial SAPO-34 and four samples targeting silicalite-1@SAPO-34 materials following 24 h, 48 h, 72 h and 144 h crystallization (with ion exchange of SAPO-34 seed crystals). Normalized intensity is plotted against the diffraction angle 2 θ .

Preparation of Mechanical Mixtures of SAPO-34 with Silicalite-1, Synthesis of Silicalite-1 at Different pH Values, and Synthesis of Silicalite-1@SAPO-34 as a Function of Crystallization Time and Hydrolysis Condensation

In Tables 4.10 and 4.11, the calculated cell parameters a, b and c, the goodness of fit, and the LVol-IB crystallite sizes are listed for prepared mechanical mixtures of commercial SAPO-34 with as-synthesised silicalite-1 under varying weight ratio, as well as for silicalite-1 and silicalite-1@SAPO-34 samples. Furthermore, a selection of the diffraction patterns after Pawley refinement is available in the Appendices (see Chapter 7.1, Figures 7.4, 7.5 and 7.6). In Table 4.10, the mechanical mixtures of commercial SAPO-34 with assynthesised silicalite-1 are catalogued according to their weight ratios. These were prepared to observe in the XRD patterns how the intensity of the diffraction peaks corresponding to the CHA and MFI phases shifts with varying weight ratios. For that reason, they should be used as references when comparing with the patterns of the attempted silicalite-1@SAPO-34 materials. From what can be gathered, the mechanical mixtures involving SAPO-34 and silicalite-1 exhibit crystalline MFI and CHA phases. This allows to create a contrast between the SAPO-34 and silicalite-1 components of the mixtures. Moreover, the diffractograms of the mechanical mixtures are sufficiently crystalline to carry out Pawley refinement. Regarding the cell parameters of all the mechanical mixtures, these do not appear to show any particular trend for both the CHA and MFI phases despite the modified weight ratios. In contrast, the LVol-IB crystallite size appears to be the lowest by far for 0.06 SAPO-34:1.0 Silicalite-1 and 0.21 SAPO-34 : 1.0 Silicalite-1 at respectively 345.26 nm and 208.33 nm. When contrasted with the remaining SAPO-34 and silicalite-1 mixtures, these tend to converge to a maximum of 4489.5 nm. This is possibly due to a crystallite size input when a sufficiently large weight ratio of SAPO-34 is fulfilled. Furthermore, a limitation from the Pawley refinement may be responsible for the maximum crystallite size.

Table 4.10: Targeted and actual zeotype phase, goodness of fit, cell parameters and crystallite size of mechanical mixtures of SAPO-34 with silicalite-1 calculated using Pawley refinement.

Sample code	Targeted/actual zeotype	Goodness of fit	Cell parameters a, b, c [Å]	LVol-IB crystallite size
	phase(s)	[-]		[nm]
0.06 SAPO- 34 : 1.0 Silicalite-1	MFI & CHA/MFI & CHA	3.576	a = b = 13.499, c = 15.127 (CHA); a = 19.937, b = 19.695, c = 13.394 (MFI)	345.26
0.21 SAPO- 34 : 1.0 Silicalite-1	MFI & CHA/MFI & CHA	3.104	a = b = 13.569, c = 14.883 (CHA); a = 19.937, b = 19.698, c = 13.395 (MFI)	208.33
0.36 SAPO- 34 : 1.0 Silicalite-1	MFI & CHA/MFI & CHA	1.487	a = b = 13.565, c = 14.864 (CHA); a = 20.035, b = 19.934, c = 13.399 (MFI)	4489.5
0.51 SAPO- 34 : 1.0 Silicalite-1	MFI & CHA/MFI & CHA	1.467	a = b = 13.558, c = 14.834 (CHA); a = 20.035, b = 19.936, c = 13.401 (MFI)	4489.5
0.66 SAPO- 34 : 1.0 Silicalite-1	MFI & CHA/MFI & CHA	2.797	a = b = 13.551, c = 14.814 (CHA); a = 19.936, b = 19.698, c = 13.399 (MFI)	4489.5
0.06 Silicalite- 1 : 1.0 SAPO-34	MFI & CHA/MFI & CHA	1.497	a = b = 13.583, c = 14.899 (CHA); a = 20.175, b = 19.851, c = 13.098 (MFI)	4484.0
0.21 Silicalite- 1 : 1.0 SAPO-34	MFI & CHA/MFI & CHA	1.625	a = b = 13.585, c = 14.890 (CHA); a = 20.058, b = 19.817, c = 13.080 (MFI)	4489.4
0.36 Silicalite- 1 : 1.0 SAPO-34	MFI & CHA/MFI & CHA	1.826	a = b = 13.588, c = 14.893 (CHA); a = 20.224, b = 19.996, c = 13.229 (MFI)	4489.5
0.51 Silicalite- 1 : 1.0 SAPO-34	MFI & CHA/MFI & CHA	1.843	a = b = 13.589, c = 14.894 (CHA); a = 19.997, b = 19.778, c = 13.257 (MFI)	4489.5
0.66 Silicalite- 1 : 1.0 SAPO-34	MFI & CHA/MFI & CHA	1.93	a = b = 13.594, c = 14.884 (CHA); a = 20.076, b = 19.857, c = 13.176 (MFI)	4489.5

As can be gathered from Table 4.11, the synthesis of silicalite-1 and silicalite-1@SAPO-34 materials has been attempted under the influence of different synthesis medium factors. Sample codes with the tag "SiO₂" correspond to reference samples which denote that TEOS in the respective reactant gel was converted to amorphous SiO₂ through hydrolysis condensation with AcOH, with no further attempt of amorphous SiO₂ being converted to

silicalite-1. In the case of the pH-dependent silicalite-1 samples, it has been determined that these cannot be synthesised with a decrease of the pH value in the reactant gel. As a result, the patterns of these samples are amorphous. On the other hand, the silicalite-1 samples obtained via hydrolysis condensation of TEOS using AcOH led to the formation of highly crystalline MFI frameworks. Out of all the attempted silicalite-1@SAPO-34 materials, only Silicalite-1@SAPO-34(24h/iPrOH+NH₃) emerges as amorphous. Apart from this, the values of goodness of fit are highly satisfactory for the crystalline samples, with the highest value standing at 2.844 for Silicalite-1@SAPO-34(48h/AcOH). Nonetheless, even if these feature CHA and MFI diffraction peaks in their XRD patterns, this does not necessarily mean that MFI@CHA materials are present; a mechanical mixture of the corresponding crystals would also display a similar pattern. With reference to the cell parameters, those from the MFI phase of the silicalite-1 samples obtained via hydrolysis condensation with AcOH diverge somewhat from the cell parameters of the MFI phase in the silicalite-1@SAPO-34 materials. In addition, the cell parameters of the CHA phase in the silicalite-1@SAPO-34 materials that were not exposed to iPrOH seem to be slightly greater than the ones of the materials that contained iPrOH in the respective reactant gels. Lastly, the LVol-IB crystallite sizes of the silicalite-1 samples are generally much lower than those of silicalite-1@SAPO-34 materials; it is interesting to observe that the LVol-IB crystallite size of SiO2@SAPO-34(AcOH), which is prior to the hydrothermal synthesis of silicalite-1@SAPO-34, is relatively low compared to that of these shell@core materials.

Table 4.11: Targeted and actual zeotype phase, goodness of fit, cell parameters and crystallite size of silicalite-1 and silicalite-1@SAPO-34 materials calculated using Pawley refinement.

Sample code	Targeted/actual zeotype	Goodness of	Cell parameters a, b, c [Å]	LVol-IB crystallite
	phase(s)	fit [-]		size [nm]
Silicalite-1(24h/pH7.05)	MFI/amorphous	-	-	-
Silicalite-1(24h/pH8.25)	MFI/amorphous	-	-	-
Silicalite-1(24h/pH9.53)	MFI/amorphous	-	-	-
Silicalite-1(24h/pH10.59)	MFI/amorphous	-	-	-
Silicalite-1@SAPO- 34(24h/iPrOH+AcOH)	MFI & CHA/MFI & CHA	1.065	a = b = 13.584, c = 14.689 (CHA); a = 20.450, b = 19.281, c = 13.107 (MFI)	4489.5
Silicalite-1@SAPO- 34(24h/iPrOH+NH ₃)	MFI & CHA/amorphous	-	-	-
Silicalite-1@SAPO- 34(24h/iPrOH)	MFI & CHA/MFI & CHA	2.61	a = b = 13.577, c = 14.684 (CHA); a = 20.345, b = 19.397, c = 13.092 (MFI)	4489.5
SiO ₂ @SAPO-34(AcOH)	CHA/CHA	1.975	<i>a</i> = <i>b</i> = 13.573, <i>c</i> = 14.825	407.76
Silicalite-1@SAPO- 34(24h/AcOH)	MFI & CHA/MFI & CHA	2.673	a = b = 13.658, c = 14.856 (CHA); a = 20.332, b = 19.735, c = 13.125 (MFI)	4489.5
Silicalite-1@SAPO- 34(48h/AcOH)	MFI & CHA/MFI & CHA	2.844	a = b = 13.677, c = 14.883 (CHA); a = 20.278, b = 19.730, c = 13.141 (MFI)	2225.3
Silicalite-1@SAPO- 34(144h/AcOH)	MFI & CHA/MFI & CHA	1.493	a = b = 13.642, c = 14.722 (CHA); a = 20.248, b = 19.674, c = 13.156 (MFI)	4489.5
SiO ₂ (AcOH)	Amorphous/amorphous	-	-	-
Silicalite-1(24h/AcOH)	MFI/MFI	2.004	a = 20.012, b = 19.919, c = 13.378	199.55
Silicalite-1(48h/AcOH)	MFI/MFI	1.65	a = 20.012, b = 19.908, c = 13.373	140.09
Silicalite-1(144h/AcOH)	MFI/MFI	1.456	a = 20.020, b = 19.907, c = 13.381	1730.7

The standard powder patterns for the MFI and CHA zeotype frameworks, as well as the recorded diffractograms for the five mechanical mixtures of commercial SAPO-34 with as-synthesised silicalite-1 under variation of the weight ratio of the former can be observed in Figure 4.10. Major diffraction peaks have been indexed with the Miller indices (*hkl*) from the *IZA-SC* database. These mechanical mixtures are arranged in such a manner, that the experimental patterns exhibit an increasing weight ratio of SAPO-34 from bottom to top. Depending on the weight ratios, the mixtures overlap to an extent with the diffraction peaks of the CHA and MFI references, e.g. (-1 1 0) and (-2 1 0) for CHA, as well as (1 0 1) and (5 0 1) for MFI. As is expected, a trend

can be detected where the intensity of the diffraction peaks associated with the CHA phase increases with rising weight ratio of SAPO-34, whereas the inverse takes place with the diffraction peaks of the MFI phase due to the relative drop in the weight ratio of silicalite-1.



Figure 4.10: XRD patterns of CHA and MFI standards, and five mechanical mixtures of commercial SAPO-34 with as-synthesised silicalite-1 under variation of the weight ratio of the former. Normalized intensity is plotted against the diffraction angle 2 θ .

Together with the CHA and MFI standard powder patterns, Figure 4.11 portrays the experimental diffractograms obtained for the five mechanical mixtures of as-synthesised silicalite-1 with commercial SAPO-34 under variation of the weight ratio of the former. As can be observed, the experimental patterns are aligned from bottom to top following a rise in the weight ratio of silicalite-1. As a consequence of the weight ratios, the diffractograms of the mixtures match more or less with the diffraction peaks belonging to the CHA and MFI references, e.g. (-1 1 0) and (-2 1 0) for CHA, as well as (1 0 1) and (5 0 1) for

MFI. Furthermore, a tendency can be confirmed where the intensity of the diffraction peaks assigned to the MFI phase grows with expanding weight ratio of silicalite-1, while the opposite occurs to the diffraction peaks of the CHA phase owing to the decline of the weight ratio of SAPO-34.



Figure 4.11: XRD patterns of CHA and MFI standards, and five mechanical mixtures of as-synthesised silicalite-1 with commercial SAPO-34 under variation of the weight ratio of the former. Normalized intensity is plotted against the diffraction angle 2 θ .

The standard powder pattern for the MFI framework and the recorded diffractograms of the four attempted pH-dependent silicalite-1 samples are illustrated in Figure 4.12. The experimental patterns are illustrated according to increasing pH value of the reactant gel from bottom to top. As can be gathered from the results, all experimental patterns with the exception of Silicalite-1(24h/pH10.59) appear completely amorphous and do not correlate whatsoever with the MFI reference. In the case of Silicalite-1(24h/pH10.59), it is possible to discern some diffraction peaks that indicate the presence of an MFI phase, e.g.

(1 0 1) and (5 0 1). Nevertheless, this sample can be dismissed as mostly amorphous since its pattern displays a quite high baseline and therefore minimal crystallinity. On balance, it can be said that hydrothermal synthesis of silicalite-1 after reducing the pH value of its reactant gel is not feasible.



Figure 4.12: XRD patterns of MFI standard and four samples targeting silicalite-1 with reduced pH value in reactant gel. Normalized intensity is plotted against the diffraction angle 2 θ .

The standard powder pattern for the CHA and MFI zeotype frameworks, as well as the recorded diffractograms for three samples targeting silicalite-1@SAPO-34 materials that contained iPrOH in their reactant gels can be observed in Figure 4.13. Judging by the three experimental patterns, Silicalite-1@SAPO-34(24h/iPrOH+NH₃) is the only sample that has become totally amorphous, with no trace left of a CHA framework. The pH values suggest that inducing hydrolysis condensation of TEOS via addition of an NH₃-solution will lead to the dissolution of the SAPO-34 framework. Regarding the other two samples, they maintain moderate crystallinity due to their somewhat low baseline and the presence of diffraction peaks that overlap satisfactorily with the CHA phase, e.g. (-1 1 0) and (-2 1 0). However, it cannot be said whether silicalite-1 has been formed since the characteristic diffraction peaks are not observable. It is possible that a very low amount has been synthesised, but which cannot be readily identified given the relatively abundant amount of SAPO-34.



Figure 4.13: XRD patterns of CHA and MFI standards, and three samples targeting silicalite-1@SAPO-34 materials with iPrOH in reactant gel. Normalized intensity is plotted against the diffraction angle 2 θ .

Together with the CHA and MFI standard powder patterns, Figure 4.14 portrays the experimental diffractograms obtained for a commercial SAPO-34 sample with condensed SiO₂ and for three attempted silicalite-1@SAPO-34 materials that did not include iPrOH in the respective reactant gels. Furthermore, the attempted silicalite-1@SAPO-34 materials also experienced different crystallization times, with a descending crystallization time starting from the top pattern. As expected, the rather crystalline sample SiO₂@SAPO-

34(AcOH) from hydrolysis condensation does not exhibit any additional diffraction peaks apart from the ones of the CHA phase, e.g. (-1 1 0) and (-2 1 0). In fact, this also applies for the attempted silicalite-1@SAPO-34 materials, which feature reasonably flat baselines and thus elevated crystallinity. In spite of the variation in crystallization time, there appears to be no major shift in the intensity of the diffraction peaks when comparing with the baseline. Once again, it is difficult to determine if silicalite-1 has been generated due to the absence of diffraction peaks of an MFI phase. An insufficient amount of silicalite-1 may appear invisible on the experimental patterns.



Figure 4.14: XRD patterns of CHA and MFI standards, commercial SAPO-34 sample with condensed SiO₂, and three samples targeting silicalite-1@SAPO-34 materials without iPrOH in reactant gel following 24 h, 48 h and 144 h crystallization. Normalized intensity is plotted against the diffraction angle 2 θ .

Figure 4.15 displays the MFI standard powder pattern as well as diffractograms from condensed SiO₂ and the three attempted silicalite-1 samples that did not have iPrOH in their reactant gels. As a reminder, the

crystallization time differs between silicalite-1 samples, with a descending crystallization time beginning from the top pattern. To begin with, it is not surprising that SiO₂(AcOH) appears amorphous since it is only the result of hydrolysis condensation of TEOS into amorphous SiO₂ via addition of AcOH. However, synthesis of the attempted silicalite-1 samples departing from SiO₂(AcOH) has shown that extremely crystalline products with flat baselines can be achieved. Their experimental patterns match extremely well with that of the MFI reference, e.g. (1 0 1) and (5 0 1). Apart from this, the crystallinity does not seem to vary above 24 h of crystallization time. Another aspect worth mentioning is that since silicalite-1 can be synthesised successfully, it could be present in the aforementioned three samples targeting silicalite-1@SAPO-34 materials without iPrOH in reactant gel following 24 h, 48 h and 144 h crystallization, although in much lower quantities compared to SAPO-34.



Figure 4.15: XRD patterns of MFI standard, condensed SiO₂, and three samples targeting silicalite-1 without iPrOH in reactant gel following 24 h, 48 h and 144 h crystallization. Normalized intensity is plotted against the diffraction angle 2 θ .

4.4.2 Scanning Electron Microscopy and Energy-Dispersive Xray Spectroscopy

Calcined Silicalite-1@SAPO-34 as a Function of Crystallization Time and TPABr Pre-Treatment with Pre-Crystallization

At resolutions of 1 and 10 µm, SEM images were recorded on commercial SAPO-34(com.), and on the attempted silicalite-1@SAPO-34 190117[A]_{..}_s@c,sol/c550 samples (3 h crystallization), 190117[B]_{..}_s@c,sol/c550 (5 h crystallization), 190117[C]_{..}_s@c,sol/c550 (7 h crystallization) and 190117[D] {..} s@c,sol/c550 (9 h crystallization), with the SAPO-34 seed crystals subjected to ion exchange prior to synthesis. A selection of these images is displayed in Figure 4.16. In the case of the sample SAPO-34(com.), its particles can be observed in images [a] and [b] being between 1 and 8 µm in length. Nevertheless, there is no direct evidence of cubic-like rhombohedral morphologies that are typical of SAPO-34 crystals²³. As for 190117[A] {...} s@c,sol/c550, its crystals are portrayed in image [c]. One crystal in particular exhibits the coffin morphology found in silicalite-1, with dimensions of 7 by 14 µm¹⁷¹. In image [d], 190117[B] {...} s@c,sol/c550 features particles with spherical morphology and diameters of about 1 to 2 µm. Apart from one coffin-shaped crystal, only spherical silicalite-1 can be recognized, which may be due to differences in apparent crystal growth rates¹⁷². Regarding 190117[C]_{...}s@c,sol/c550, the sample possesses in image [e] both spherical particles and coffin-shaped crystals, with a noticeable representative of the latter being 9 by 10 µm. Finally, image [f] shows spherical and coffin morphologies in 190117[D] {...} s@c,sol/c550, but in addition there is evidence of amorphous material which has accumulated on the product. This may be related to the longer crystallization time. All in all, it is possible to observe silicalite-1 in the attempted silicalite-1@SAPO-34 samples. Furthermore, there appears to be a greater amount of spherical particles with higher crystallization times. Nevertheless, SAPO-34 crystals are not readily visible because of the absence of cubic-like rhombohedral crystals. Because

spherical and coffin-shaped particles of silicalite-1 are not seen to be clearly covering the surface of cubic-like rhombohedral crystals of SAPO-34, it is not possible to establish via the SEM images if and to what extent a silicalite-1 shell has been generated on SAPO-34 seed crystals^{23,171}.



[b]



Figure 4.16: SEM images of commercial SAPO-34 [a,b], and of attempted silicalite-1@SAPO-34 samples 190117[A]_{...}_s@c,sol/c550 (3 h crystallization) [c], 190117[B]_{...}s@c,sol/c550 (5 h crystallization) [d], 190117[C]_{...}_s@c,sol/c550 crystallization) [e] (7 h and 190117[D]_{...}s@c,sol/c550 (9 h crystallization) [f] (ion-exchanged SAPO-34 seed crystals).

Synthesis of Silicalite-1@SAPO-34 as a Function of Crystallization Time and Hydrolysis Condensation

At resolutions of 1 and 10 µm, SEM images were recorded on silicalite-1 (24 h crystallization) and on the attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-34(24h/AcOH), Silicalite-1@SAPO-34(48h/AcOH) and Silicalite-1@SAPO-34(144h/AcOH), with the absence of iPrOH in the respective reactant gels. A selection of these images is displayed in Figure 4.17. In the case of silicalite-1 (24 h crystallization), its crystals are portrayed in image [a]. These exhibit the spherical morphology found in silicalite-1, with diameters of about 0.5 to 2 µm¹⁷¹. In image [b], Silicalite-1@SAPO-34(24h/AcOH) features fractured particles and amorphous material agglomerated on what appears to be fragmented crystals of SAPO-34, which is meant to display a cubic-like rhombohedral morphology²³. Moreover, the individual SAPO-34 crystals possess dimensions of up to 8 µm. Regarding Silicalite-1@SAPO-34(48h/AcOH), the sample possesses in image [c] these fragmented SAPO-34 crystals, but also a fibrous or threadlike overgrowth on them which may be indicative of silicalite-1 and/or amorphous material. SAPO-34 crystals present in here reach lengths of up to about 8 µm as well. Finally, image [d] shows a greater prevalence of this fibrous overgrowth on fragmented SAPO-34 crystals. This may be related to the longer crystallization time. All in all, it is not possible to observe the characteristic morphology of silicalite-1 in the attempted silicalite-1@SAPO-34 samples. On the other hand, there appears to be a trend indicating a greater volume of threadlike overgrowth with higher crystallization times; this threadlike morphology is recognisable in the centre of image [d]. Besides this, SAPO-34 crystals do not manifest an intact cubic-like rhombohedral morphology. For this reason, it is not possible to establish via the SEM images if and to what extent a silicalite-1 shell has been generated on the SAPO-34 seed crystals.



Figure 4.17: SEM images of silicalite-1 (24 h crystallization) [a] and of attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-34(24h/AcOH) [b], Silicalite-1@SAPO-34(48h/AcOH) [c] and Silicalite-1@SAPO-34(144h/AcOH) [d] (without iPrOH in reactant gel).

Cu(II) Ion Exchange of SAPO-34 and of Silicalite-1@SAPO-34 derived from Hydrolysis Condensation

EDS spectra coupled with SEM images at resolutions of 10 and 20 μ m were recorded on Cu(II) ion-exchanged commercial SAPO-34 and on three silicalite-1@SAPO-34 samples derived from hydrolysis condensation of TEOS with acetic acid to assess the chemical composition of these products. The chemical composition results are available in Figure 4.18, which contains the atomic percentage of the assessed elements. In addition, a selection of the EDS and SEM images with elemental mapping in predefined areas is available

in the Appendices (see Chapter 7.2, Figure 7.10). It can be gathered that Cu/SAPO-34(c900) exhibits the lowest atomic percentage for Si, which can be explained by the fact that the sample was not subjected to hydrolysis condensation of TEOS with acetic acid. Concerning the silicalite-1@Cu/SAPO-34 samples, the values of Si, Al, P and Cu tend to decrease with longer crystallization times. In the case of Si, Al and P, the drop in atomic percentage is brought about by the targeted growth of a silicalite-1 shell on SAPO-34 seed crystals during longer sessions of hydrothermal synthesis of silicalite-1@SAPO-34 materials. As for Cu, its incorporation appears to be greater with lower crystallization times. One reason may be that a higher atomic percentage of Al enables more Brønsted acid sites where exchange for Cu²⁺ ions can occur. Nevertheless, there is no clear indication as to what kinds and proportions of Cu species are present in the samples. To probe this feature, XPS and UV-Vis spectroscopy were employed.



Figure 4.18: Atomic percentage of the EDS assessed elements (Si, Al, P, O, Cu) for Cu(II) ion-exchanged commercial SAPO-34 and three samples targeting silicalite-1@SAPO-34 materials derived from hydrolysis condensation following 24 h, 48 h and 144 h crystallization.

4.4.3 X-ray Photoelectron Spectroscopy

Mechanical Mixtures of SAPO-34 with Silicalite-1, and Calcined Silicalite-1@SAPO-34 as a Function of Crystallization Time and TPABr Pre-Treatment with Pre-Crystallization

X-ray photoelectron spectra were recorded for five mechanical mixtures of commercial SAPO-34 and as-synthesised silicalite-1 with different weight ratios to compare XPS analysis results with those of commercial SAPO-34 and of attempted silicalite-1@SAPO-34 materials that had their core material subjected to ion exchange and drying in the oven. The surface composition results are available in Figure 4.19, which contains the atomic percentage of the assessed elements. In addition, a selection of the XPS spectra with highlighted element scan ranges is available in the Appendices (see Chapter 7.3, Figure 7.11). It can be gathered that commercial SAPO-34 exhibits for Si the lowest atomic percentage, and for AI and P the highest atomic percentages. For the attempted silicalite-1@SAPO-34 materials, both the values of AI and P tendentially decrease with longer crystallization times since SAPO-34 seed crystals are added into a pre-crystallization silicalite-1 slurry for the subsequent hydrothermal synthesis of a growing silicalite-1 phase fraction. Nevertheless, if successful synthesis of silicalite-1@SAPO-34 materials were to have been achieved, these values should be equal to or close to zero. Due to the fact that only the SAPO-34 core should feature these elements and that XPS would only allow surface composition analysis of the silicalite-1 shell in the exclusive presence of silicalite-1@SAPO-34, it would appear that shell@core materials are not available here. Moreover, it should be pointed out that the sample with the longest crystallization time has the lowest values for AI and P. In view of this, insufficient crystallization time may be the cause for not achieving definitive shell@core formation. Another possibility is that formation of the shell did take place, but it is not thick enough to hide all the core. Regarding the mechanical mixtures, these display an upwards trend for the values of AI and P, whereas the atomic percentage of Si shows a steady decline. Lastly, the atomic percentages of P and Al from 0.36 SAPO-34 : 1.0 Silicalite-1 seem to converge best with those of the targeted silicalite-1@SAPO-34 materials.



Figure 4.19: Atomic percentage of the XPS assessed elements (Si, AI, P, O) for five mechanical mixtures of commercial SAPO-34 and as-synthesised silicalite-1 with different weight ratios, and for commercial SAPO-34 and four calcined samples targeting silicalite-1@SAPO-34 materials following 3 h, 5 h, 7 h and 9 h crystallization (with ion exchanged and oven-dried SAPO-34 seed crystals).

Synthesis of Silicalite-1@SAPO-34 as a Function of Crystallization Time and Hydrolysis Condensation

X-ray photoelectron spectra were recorded for commercial SAPO-34 and for the attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-34(24h/AcOH), Silicalite-1@SAPO-34(48h/AcOH) and Silicalite-1@SAPO-34(144h/AcOH), following hydrolysis condensation with the absence of iPrOH in the respective reactant gels. The surface composition results are available in Figure 4.20, which contains the atomic percentage of the assessed elements. In addition, a selection of the XPS spectra with highlighted element scan ranges is available in the Appendices (see Chapter 7.3, Figure 7.12). It can be gathered that commercial SAPO-34 exhibits for Si the lowest atomic percentage, and for AI and P the highest atomic percentages. Regarding the attempted silicalite-1@SAPO-34 materials, both the values of AI and P tend to decrease with longer crystallization times. This is because SAPO-34 seed crystals, which have been subjected to hydrolysis condensation of TEOS with acetic acid, are added into a final reactant gel for posterior hydrothermal synthesis of a growing silicalite-1 phase fraction. If successful synthesis of silicalite-1@SAPO-34 materials were to have been achieved, these values should be converging towards zero. Taking this into account, insufficient crystallization time may be the cause for not achieving definitive shell@core formation.



Figure 4.20: Atomic percentage of the XPS assessed elements (Si, Al, P, O) for commercial SAPO-34 and attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-34(24h/AcOH), Silicalite-1@SAPO-34(48h/AcOH) and Silicalite-1@SAPO-34(144h/AcOH) (without iPrOH in reactant gel).

4.4.4 Ultraviolet-Visible Spectroscopy

Cu(II) Ion Exchange of SAPO-34 and of Silicalite-1@SAPO-34 derived from Hydrolysis Condensation

UV-Vis spectroscopic analysis was performed on Cu(II) ion-exchanged commercial SAPO-34 and on three silicalite-1@SAPO-34 samples derived from hydrolysis condensation of TEOS with acetic acid to assess the coordination state of Cu species in the SAPO-34 phase framework. The UV-Vis spectra of the abovementioned samples are illustrated in Figure 4.21. The main charge transfer band corresponding to charge transitions from O_{zeolite} to Cu²⁺ ions can be observed at about 240 nm¹⁶³. In other words, it can be allocated to the interaction of Cu species with the Brønsted acid sites in the SAPO-34 phase framework. Whereas the incorporation of Cu in Brønsted acid sites for all silicalite-1@Cu/SAPO-34 samples appears to be equally high regardless of the crystallization time, this does not appear to be the case for Cu/SAPO-34(c550). Nonetheless, all samples exhibit a broad absorption band stretching from 600 to 800 nm which can be assigned to electron d-d transitions of isolated Cu²⁺ ions and distorted octahedral Cu²⁺ surrounded by oxygen in CuO particles^{163,173}. Besides this, charge transfer bands that are observable in the range from 350 to 450 nm correspond to O-Cu-O and Cu-O-Cu complexes¹⁷⁴. Even so, these spectra suggest that even if a share of Cu species may be part of CuO particles on the external surface of the samples, it is possible for Cu²⁺ ions to migrate to the Brønsted acid sites during ion exchange. For this reason, it can be said that systems containing a SAPO-34 phase with Cu²⁺ cations in the zeolite exchange sites can be produced.



Figure 4.21: UV-Vis spectra of Cu(II) ion-exchanged commercial SAPO-34 and three samples targeting silicalite-1@SAPO-34 materials derived from hydrolysis condensation following 24 h, 48 h and 144 h crystallization.

4.5 Conclusions and Discussion

Regarding the three attempted as-synthesised shell@core materials consisting of silicalite-1@CoAPO-34 where synthesis was a function of seed crystal mass per reactant gel volume, these are essentially amorphous and do not exhibit the hybrid pattern of a MFI@CHA material. As for the four targeted as-synthesised shell@core materials based on silicalite-1@SAPO-34 that were affected by the same function, the diffraction patterns of 160816_{...}_comp,sol and 280916_{...}_comp,sol correlate well respectively with the MFI and CHA references. Despite the other two silicalite-1@SAPO-34 materials presenting weak crystallinity, 220916_{...}_comp,sol features a few peaks correspondent to an MFI framework, whereas 270916_{...}_comp,sol has an analogous situation with the CHA standard. Even so, no proper MFI@CHA material was attained. There appears to be a phase transition as a function of the seed

crystal mass per gel volume, yet it remains to be confirmed. Besides this, a reason why the synthesis of this class of composite failed in the silicalite-1@CoAPO-34 and silicalite-1@SAPO-34 series may lie in the high pH values of the reactant gels prior to crystallization.

Judging from the XRD patterns, it can be concluded that the synthesis of samples with the MFI and CHA frameworks was successful where the approach of pre-treating the SAPO-34 crystals via ion exchange with TPABr followed by pre-crystallization was employed. Carrying out ion exchange as indicated by Razavian and Fatemi may have protected the SAPO-34 seed crystals from the strong basic synthesis media of the pre-crystallization silicalite-1 slurry⁷². As for the calcined analogous samples, these manage to maintain both framework topologies. However, one of the attempted silicalite-1@SAPO-34 materials, namely 190117[D]-{...}s@c,sol/c550, manifests a lower intensity for its CHA framework in contrast to the other calcined samples. The longer crystallization time of this sample may be responsible for how calcination will impact the framework ratio viewed on the diffraction patterns.

In contrast to the XRD patterns of attempted silicalite-1@SAPO-34 materials which involved ion exchange and pre-crystallization, synthesis of silicalite-1@SAPO-34 materials without pre-crystallization resulted only in diffractograms that exhibit amorphous patterns without any overlap to the CHA and MFI references. This is regardless of whether the SAPO-34 crystals were pre-treated via ion exchange with TPABr or not. In the case of the samples where the core material did not undergo ion exchange, this presumably accelerated the disintegration of the SAPO-34 framework by the strong basic synthesis medium (pH \approx 11). With regard to the attempted silicalite-1@SAPO-34 materials with a pre-treated core material as precursor, it is difficult to pinpoint the origin of the problem because the attempted shell@core materials which underwent pre-crystallization were synthesised using ion exchanged SAPO-34 and feature CHA and MFI diffraction peaks in their diffraction patterns. It may lie in the fact that, in contrast to the oven dried pre-treated SAPO-34 of the shell@core materials subjected to pre-crystallization, this batch of attempted shell@core materials was excluded from pre-crystallization and incorporated in its synthesis SAPO-34 which had been dried at room temperature after ion exchange. To rule out other possible issues, an XRD

pattern of double ion exchanged commercial SAPO-34 was obtained that clearly matches with the CHA reference. Furthermore, XRD patterns of silicalite-1 after different crystallization times were recorded to determine that there were no flaws in the precursors or in the hydrothermal synthesis procedure.

In another synthesis approach for silicalite-1@SAPO-34 materials, hydrolysis condensation of TEOS with acetic acid was employed as an intermediary step prior to hydrothermal synthesis. Products targeting silicalite-1@SAPO-34 which underwent this synthesis procedure are Silicalite-1@SAPO-34(24h/AcOH), Silicalite-1@SAPO-34(48h/AcOH) and Silicalite-1@SAPO-34(144h/AcOH), with the absence of iPrOH in the respective reactant gels. Given the fact that the CHA framework topology in these products appears intact in their respective XRD patterns, it is possible that amorphous SiO₂ from condensation of TEOS may have deposited onto the SAPO-34 crystals and protected these from disintegration in the strong basic synthesis medium $(pH \approx 14)$ of the final reactant gel. Even though diffraction peaks belonging to an MFI phase are not readily visible, a minimal amount of silicalite-1 may have been formed which appears invisible on the experimental patterns due to its comparatively low weight ratio. Furthermore, there appears to be no major shift in the intensity of the diffraction peaks when comparing with the baseline despite the varied crystallization time.

Regardless of the results from XRD, this analytical technique alone is not enough to confirm the existence of shell@core assemblies. It is necessary to complement the results from the XRD patterns with those from SEM images and XPS spectra to establish whether the synthesis of silicalite-1@SAPO-34 materials was successful. Concerning the SEM images, spherical particles and coffin-like crystals of silicalite-1, which are a result of differing apparent crystal growth rates, can be easily identified. On the other hand, it is difficult to observe SAPO-34 crystals because there is not a cubic-like rhombohedral morphology which can be readily recognized. In view of this, it is not feasible to determine alone from the SEM images whether silicalite-1@SAPO-34 materials are present. Following Cu(II) ion exchange, EDS spectra of commercial SAPO-34 and the three attempted silicalite-1@SAPO-34 samples derived from hydrolysis condensation of TEOS with acetic acid confirm the existence of Si, AI, P, O and Cu, implying that Cu can be incorporated in the SAPO-34 phase framework.

Furthemore, it is difficult to observe the characteristic morphology of silicalite-1 in the attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-34(24h/AcOH), Silicalite-1@SAPO-34(48h/AcOH) and Silicalite-1@SAPO-34(144h/AcOH). However, there appears to be a greater volume of fibrous overgrowth on seemingly fragmented SAPO-34 crystals with higher crystallization times; SAPO-34 crystals do not manifest an intact cubic-like rhombohedral morphology. Because of this, it is not possible to reach a conclusion on whether silicalite-1@SAPO-34 materials have been formed.

XPS displays the variation of the atomic percentages of Si, Al, P and O through mechanical mixtures of commercial SAPO-34 and as-synthesised silicalite-1 with different weight ratios. These are put in contrast with the values of commercial SAPO-34 and attempted silicalite-1@SAPO-34 materials that had their core material subjected to ion exchange and drying in the oven. As expected, commercial SAPO-34 displays the lowest atomic percentage for Si, and the highest atomic percentages for AI and P among the analyzed samples. With respect to the attempted silicalite-1@SAPO-34 samples, there is no evidence of shell@core materials because the values of P and AI are not equal to or close to zero. However, the partial formation of a shell cannot be fully excluded. In the case of the mechanical mixtures, the value of Si declines steadily with increasing SAPO-34 weight ratio, whereas the values of AI and P show the opposite trend. Furthermore, the atomic percentages of P and Al from 0.36 SAPO-34 : 1.0 Silicalite-1 appears to best match the values of both elements from the attempted silicalite-1@SAPO-34 materials. On balance, the synthesis of silicalite-1@SAPO-34 materials was not successful.

Further XPS spectra were recorded to measure the variation of the atomic percentages of Si, Al, P and O for commercial SAPO-34 and for the attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-34(24h/AcOH), Silicalite-1@SAPO-34(48h/AcOH) and Silicalite-1@SAPO-34(144h/AcOH). In the case of commercial SAPO-34, it features the lowest atomic percentage for Si, and the highest atomic percentages for Al and P among the analyzed samples. As for the attempted silicalite-1@SAPO-34 samples, their values for Al and P tend to drop with higher crystallization times. If ideal silicalite-1@SAPO-34 materials were to be obtained, the values of these two elements should be approaching zero. The question remains whether partial silicalite-

1@SAPO-34 materials have been generated.

Following Cu(II) ion exchange, UV-Vis spectra of commercial SAPO-34 and three silicalite-1@SAPO-34 samples derived from hydrolysis condensation of TEOS with acetic acid indicate that Cu²⁺ ions can be incorporated in the Brønsted acid sites of the SAPO-34 phase framework even in the presence of a silicalite-1 shell around the core. Even though a portion of the Cu species consists of CuO particles on the external surface of the samples, these can be further dispersed as Cu²⁺ ions to the zeolite exchange sites via hydrothermal treatment¹⁶³.

Chapter 5: Investigation of Synthesis Methods for Shell@Core Structures with SSZ-13, and Contrast with Analogous Zeolite Blends

5.1 Chapter Overview

In this chapter, shell@core synthesis variations for compositions involving SSZ-13, an aluminosilicate material that is isostructural to the SAPO-34 zeolite and which also features application in SCR and MTO catalysis, were investigated to understand the underlying gel chemistry and increase the stability of these structures. So far, it has been found that establishing suitable synthesis conditions for the coexistence of the shell and core is critical. For instance, the synthesis of aluminosilicate zeolites usually takes place under alkaline conditions, whereas the pH value of the SAPO-34 reactant gel lies in the neutral region. As a result of the considerable difference in the pH value of the reactant gels for core and shell zeolites, identifying effective pre-treatment methods for core crystals is decisive for the protection of these crystals in the synthesis medium and the formation of composites. For example, one strategy would be exchanging zeolite seeds with SDA molecules to preserve the core surface during shell@core synthesis.

The main concern of study is how the crystallinity, structural properties and stability are affected by changing synthesis parameters. To address these issues, modification of the surface structure of SSZ-13 has been suggested by growing a continuous hydrophobic silicalite-1 shell over SSZ-13 core crystals which protects the core from excessive water vapour in the exhaust gas during SCR while preserving the desired properties. To prepare these shell@core compositions, SSZ-13 was utilised as seed crystal in silicalite-1 reactant gels under different crystallization times. Moreover, pre-treatment of core crystals was carried out via hydrolysis condensation of TEOS with acetic acid onto them prior to synthesis of shell@core systems. To determine whether an isostructural shell can be grown more easily over a core with the same framework, hydrothermal synthesis of SSZ-13@SAPO-34 materials was also attempted by directly adding SAPO-34 seed crystals into the SSZ-13 reactant gel. Besides this, recrystallization of SSZ-13 was attempted from a CHA to an MFI zeolite topology, in other words to ZSM-5. This was done to examine the possibility of recrystallizing the framework of an SSZ-13 shell to an MFI topology in the case of SSZ-13@SAPO-34 materials. Finally, laboratory-based characterisation techniques were employed to establish how the gel chemistry affects shell@core type nanoporous systems.

5.2 Introduction

NH₃-SCR is considered an effective solution for decreasing NO_x emissions from exhausts of stationary and mobile diesel engines⁹². Vanadium based catalysts have been studied in depth and used previously as monolith converters in diesel vehicles to curtail NO_x emissions⁹³. Even so, V-based catalysts do possess specific disadvantages, for instance weak SCR activity at mild temperatures, thermal deactivation, robust activity for oxidation of SO₂ to SO₃, toxicity and disposal difficulties⁹⁴. Moreover, V-based catalysts have been slowly vanishing from use in SCR technology due to the rise of zeolite-based catalysts in this field of application^{99,100}. Currently, V-based catalysts in NH₃-SCR processes are vastly outnumbered by Cu/Fe-zeolites⁹⁷. Cu-SSZ-13 and Cu-SAPO-34, which display a small-pore CHA framework exchanged with copper ions, feature exceptional resistance to high temperatures during the regeneration of the DPF found upstream of the SCR unit¹⁰³.

Compared to other large or mesopore Cu-based zeolite catalysts, Cu-CHA catalysts such as Cu-SAPO-34 and Cu-SSZ-13 are microporous zeolites that show a ~0.38 nm pore size and garner more attention because of their better hydrothermal stability and stronger NH₃-SCR activity¹²⁵. NO conversion in reaction trials involving Cu-CHA catalysts stretches from 90 to 100% in a temperature range between 250 and 450°C. Conversion stays above 80% even after hydrothermal aging of the catalysts at 800°C¹²⁶. This also applies to Cu-SAPO-34 and Cu-SSZ-13¹²⁵. Any Al(OH)₃ resulting from dealumination is estimated to have a kinetic diameter of 5.03 Å and tend to be trapped in the small pores. Therefore, hydrothermal aging can occur while dealumination is simultaneously curbed¹²⁵.

According to Niu et al., the NH₃-SCR activity and hydrothermal stability of Cu-SAPO-34 depend on the framework pore properties, distribution of Cu species, acidity, and stability of the structure. When calcining the zeolite from 500 to 700°C, it was observed that its surface area, pore volume, and structure crystallinity increased within this temperature range, only to then collapse at 800°C¹¹⁹. Furthermore, experiments indicate that Cu-SAPO-34 can maintain superb NH₃-SCR activity after being calcined at 700°C. As a matter of fact, the catalyst exhibits over 90% NO_x conversion from 225 to 400°C after being subjected to hydrothermal aging at 800°C for 16 h¹¹⁹. In a separate study, Wang et al. report that both Cu-SSZ-13 and Cu-SAPO-34 can retain their performance after undergoing hydrothermal aging at 750°C for 16 h. As opposed to Cu-SAPO-34, Cu-SSZ-13 experiences a substantial decline in crystallinity, active Cu sites and SCR performance following hydrothermal aging at 800°C for 16 h¹²¹. The reason for this discrepancy is believed to be the residual surface Cu stemming from synthesis which migrates into the SAPO-34 pores after being subjected to elevated temperatures, leading to the formation of additional isolated Cu²⁺ sites and successive aggregation into clusters.

ETO and MTO processes can be catalysed successfully by various protonated zeolites or zeotype materials. A standard industrial MTO catalyst is SAPO-34, which offers up to 80% total carbon yield of ethylene and propylene¹³⁶. Moreover, its CHA framework is one of the noteworthy zeotype topologies that can be effortlessly synthesised in the form of silicoaluminophosphate (SAPO-34) and aluminosilicate (SSZ-13) analogues. Regarding SSZ-13, its acidity has been reported to be higher than that of SAPO-34¹³⁷. For this reason, a greater olefin production rate and retention of aromatics in catalyst pores has been ascribed to SSZ-13, therefore lowering the optimal operation temperature¹³⁸.

SSZ-13 shares the same CHA framework as SAPO-34 and manifests also a hydrophilic behaviour. Since SSZ-13 has also been tested successfully for SCR, it is believed that the idea of growing a silicalite-1 shell may be extended to this aluminosilicate zeolite to shield it from water and enhance its stability as in the case of SAPO-34. In view of this, stable shell@core structures

from SSZ-13 (core) and silicalite-1 (shell) were targeted. Moreover, hydrothermal synthesis of SSZ-13@SAPO-34 systems was also carried out to assess if an SSZ-13 shell can form more readily over a SAPO-34 core given the fact that they are isostructural to one another. Lastly, recrystallization of the CHA framework topology of SSZ-13 to the MFI type was also delved into to determine whether this can be extended to SSZ-13@SAPO-34 systems. By employing laboratory-based characterisation techniques, it was possible to correlate synthesis parameters with structural properties.

5.3 Experimental

Hydrothermal synthesis of SSZ-13@SAPO-34 and silicalite-1@SSZ-13 materials was targeted under variation of parameters, i.e. crystallization time and pre-treatment of core crystals by way of hydrolysis condensation of TEOS with acetic acid. The objective is to identify which synthesis conditions produce shell@core systems with optimal characteristics. Furthermore, recrystallization of SSZ-13 to ZSM-5, which has an MFI framework, was pursued in the presence and absence of condensed SiO₂. Besides this, mechanical mixtures of SSZ-13 and SAPO-34 were prepared with different weight ratios to compare analysis results with those of attempted SSZ-13@SAPO-34 materials.

5.3.1 Synthesis

Synthesis of SSZ-13@SAPO-34 as a Function of Crystallization Time, and Preparation of Mechanical Mixtures of SSZ-13 with SAPO-34

In the first stage, hydrothermal synthesis of shell@core materials consisting of SSZ-13@SAPO-34 was carried out to assess the feasibility of generating an isostructural shell over a core with the same CHA framework. For the synthesis of the SSZ-13 shell, the following molar ratio was used to prepare the SSZ-13 reactant gel in a PTFE beaker under stirring at room temperature:

• 1 AI : 4 Na : 20 Si : 4 T2 : 880 H₂O,

with AI(OH)₃ as AI-species [100 wt%, Sigma-Aldrich], NaOH as Na-species

[98.3 wt%, Fisher Chemical], TEOS as Si-species [98 wt%, Sigma-Aldrich], T2 as the template trimethyl-adamantylammonium hydroxide (TMAdaOH) [25 wt%, ZeoGen] and deionised water being employed as precursors¹⁷⁵.

For this approach of synthesising SSZ-13@SAPO-34 samples, NaOH, TMAdaOH and deionised water were combined at room temperature and stirred for 1 h. TEOS was added to the mixture, and then seed crystals of commercial SAPO-34 were utilized as core material and introduced into the reactant gel at a ratio of 1 g of SAPO-34 per 10.5 ml of SSZ-13 gel, which was further stirred for 1 h. This was followed by addition of Al(OH)₃ and ageing of reactant mixture for 24 h under stirring. 21 ml Teflon-lined steel autoclaves were then filled half-way with the reactant mixture, which was allowed to crystallize in a pre-heated oven at 160°C for 24 h, 48 h, 120 h and 144 h. For the purpose of comparison, a separate SSZ-13 reactant gel with the same molar ratio but without SAPO-34 was prepared and aged as well at room temperature for 24 hours. This was followed by crystallization in 45 ml Teflon-lined steel autoclaves at 160°C for 144 h. Table 5.1 summarizes the synthesis plan for the SSZ-13 and SSZ-13@SAPO-34 materials as a function of crystallization time.

Table 5.1: Performed synthesis plan of SSZ-13 and SSZ-13@SAPO-34 materials as a function of crystallization time.

Sample code	Crystallization time [h]
270917_{}_sol [SSZ-13(24h-age/144h)]	144
190917[A]_{}_s@c,sol [SSZ-13@SAPO-34(24h-age/24h)]	24
190917[B]_{}_s@c,sol [SSZ-13@SAPO-34(24h-age/48h)]	48
190917[C]_{}_s@c,sol [SSZ-13@SAPO-34(24h-age/120h)]	120
190917[D]_{}_s@c,sol [SSZ-13@SAPO-34(24h-age/144h)]	144

After crystallization, autoclaves were placed in a water bath to cool down to room temperature and the products were removed from the autoclaves. All crystallization products were then suspended in water and left to precipitate in an ultrasonic bath for one hour, which was followed by decantation. After this, the precipitates were transferred into centrifuge tubes, centrifuged thrice and then dried in an oven at 110°C overnight.

Furthermore, five mechanical mixtures of as-synthesised SSZ-13 with

commercial SAPO-34 were prepared with different weight ratios to compare analysis results with those of attempted SSZ-13@SAPO-34 materials. These are specified in Table 5.2.

Table 5.2: Mechanical mixtures of as-synthesised SSZ-13 with commercial SAPO-34 according to employed weight ratios.

Sample code	Weight ratio of SSZ-13 [-]	Weight ratio of SAPO-34 [-]
0.06 SSZ-13 : 1.0 SAPO-34	0.06	
0.21 SSZ-13 : 1.0 SAPO-34	0.21	
0.36 SSZ-13 : 1.0 SAPO-34	0.36	1.0
0.51 SSZ-13 : 1.0 SAPO-34	0.51	
0.66 SSZ-13 : 1.0 SAPO-34	0.66	

Synthesis of Silicalite-1@SSZ-13 as a Function of Crystallization Time and Hydrolysis Condensation

The second stage of hydrothermal synthesis of shell@core materials focused on silicalite-1@SSZ-13 and was performed to determine if the surface hydrophobicity of SSZ-13 can be adjusted by generating a silicalite-1 shell around SSZ-13 core crystals. Here, hydrolysis condensation of TEOS with acetic acid was employed as an intermediary step for the hydrothermal synthesis of silicalite-1@SSZ-13 samples. The following molar ratio was used for the hydrolysis condensation reaction of TEOS:

• 1 TEOS : 1 AcOH : 4 H₂O.

First, 18 g TEOS was added in a Teflon beaker, with 3 g of assynthesised SSZ-13 being suspended in the beaker (ratio of 1 g of SSZ-13 per 10.5 ml of final reactant gel) for the preparation of silicalite-1@SSZ-13 and allowed to stir at room temperature for 10 min; whilst stirring, this was followed by the dropwise addition of 21.19 g acetic acid (96 wt%) diluted with 4.89 g deionised water in the beaker and further stirring for 20 min. Next, the product slurry was transferred into centrifuge tubes, centrifuged four times and then dried in an oven at 110°C overnight. After drying, the centrifugates were placed in a Teflon beaker and diluted with a solution of 14.42 g deionised water and 23.08 g TPAOH (1.0 M) based on the molar ratio of the silicalite-1 reactant gel; the reactant mixture was left stirring at room temperature for 1 h. 21 ml Teflonlined steel autoclaves were then filled half-way with the resultant gel, which was allowed to crystallize in a pre-heated oven at 170°C for 24 h, 48 h and 144 h. Table 5.3 summarizes the synthesis plan for the silicalite-1@SSZ-13 materials as a function of synthesis medium and crystallization time.

Table 5.3: Performed synthesis plan of silicalite-1@SSZ-13 materials as a function of synthesis medium and crystallization time.

Sample code	Synthesis medium factor	Crystallization time [h]
281117[A]_{}s@c,sol [Silicalite-1@SSZ-13(24h/AcOH)]	AcOH	24
281117[B]_{}_s@c,sol [Silicalite-1@SSZ-13(48h/AcOH)]	AcOH	48
281117[C]_{}_s@c,sol [Silicalite-1@SSZ-13(144h/AcOH)]	AcOH	144

After crystallization, autoclaves were placed in a water bath to cool down to room temperature and the products were removed from the autoclaves. All crystallization products were then suspended in water and left to precipitate in an ultrasonic bath for one hour, which was followed by decantation. After this, the precipitates were transferred into centrifuge tubes, centrifuged thrice and then dried in an oven at 110°C overnight.

Recrystallization of SSZ-13 (CHA) to ZSM-5 (MFI) as a Function of Recrystallization Time and Hydrolysis Condensation

In the third stage, recrystallization of commercial SSZ-13 to ZSM-5 was pursued to establish whether a CHA framework topology can be converted to an MFI type. Two approaches were taken for the recrystallization of SSZ-13 to ZSM-5, with the first and second approach involving respectively the absence and presence of condensed SiO₂. For the first approach, 3 g of seed crystals of SSZ-13 from a commercial supplier were placed in a Teflon beaker (ratio of 1 g of SSZ-13 per 10.5 ml of final reactant gel) and diluted with a solution of 14.42 g deionised water and 23.08 g TPAOH (1.0 M) based on the molar ratio of the silicalite-1 reactant gel; the reactant mixture was left stirring at room temperature for 1 h. 21 ml Teflon-lined steel autoclaves were then filled half-way with the resultant gel, which was allowed to crystallize in a pre-heated oven at 170°C for 24 h, 48 h and 144 h.

For the second approach, hydrolysis condensation of TEOS with acetic
acid was performed as an intermediary step for the recrystallization of SSZ-13 to ZSM-5. The following molar ratio was used for the hydrolysis condensation reaction of TEOS:

• 1 TEOS : 1 AcOH : 4 H₂O.

To begin with, 18 g TEOS was poured into a Teflon beaker; whilst stirring, this was followed by the dropwise addition of 21.19 g acetic acid (96 wt%) diluted with 4.89 g deionised water in the beaker and further stirring for 20 min. Next, the product slurry was transferred into centrifuge tubes, centrifuged four times and then dried in an oven at 110°C overnight. After drying, the centrifugates were placed in a Teflon beaker, mixed with 3 g of commercial SSZ-13 (ratio of 1 g of SSZ-13 per 10.5 ml of final reactant gel) and diluted with a solution of 14.42 g deionised water and 23.08 g TPAOH (1.0 M) based on the molar ratio of the silicalite-1 reactant gel; the reactant mixture was left stirring at room temperature for 1 h. 21 ml Teflon-lined steel autoclaves were then filled half-way with the resultant gel, which was allowed to crystallize in a pre-heated oven at 170°C for 24 h, 48 h and 144 h. The recrystallization plan for SSZ-13 to ZSM-5 is available in Table 5.4 and appears as a function of synthesis medium and crystallization time.

Table 5.4: Performed recrystallization plan of SSZ-13 to ZSM-5 as a function of synthesis medium and crystallization time.

Sample code	Synthesis medium factor	Crystallization time [h]
270218[A]_{}_sol [ZSM-5(SSZ-13-recryst. 24h)]	-	24
270218[B]_{}_sol [ZSM-5(SSZ-13-recryst. 48h]	-	48
270218[C]_{}_sol [ZSM-5(SSZ-13-recryst. 144h]	-	144
050318[A]_{}_sol [ZSM-5(SSZ-13-recryst. 24h/AcOH)]	AcOH	24
050318[B]_{}_sol [ZSM-5(SSZ-13-recryst. 48h/AcOH)]	AcOH	48
050318[C]_{}_sol [ZSM-5(SSZ-13-recryst. 144h/AcOH)]	AcOH	144

After crystallization, autoclaves were placed in a water bath to cool down to room temperature and the products were removed from the autoclaves. All crystallization products were then suspended in water and left to precipitate in an ultrasonic bath for one hour, which was followed by decantation. After this, the precipitates were transferred into centrifuge tubes, centrifuged thrice and then dried in an oven at 110°C overnight.

5.3.2 Characterisation

Regarding characterisation, powder X-ray diffraction (PXRD) patterns of samples in borosilicate glass capillaries were recorded using a Stoe system with Cu-K_{a1} radiation (wavelength $\lambda = 1.5406$ Å) in the 2 θ diffraction angle range of 5 to 50°. On the basis of the diffractograms from PXRD, crystallographic properties of the samples were analysed. To begin with, the Bruker EVA software was used to establish phase ID. An input file with the xyfile of the diffractogram was then created via the program *jEdit* and loaded to the crystallography program Topas for a Pawley refinement with polynomial fitting of the background to the pattern. An output file is then generated with the calculated values for the cell parameters, the goodness of fit and the integral breadth based volume weighted column height as crystallite size. However, these values are more reliable if the samples have a high phase purity and crystallinity, which is why the goodness of fit is also taken into consideration. Any amorphous phase is regarded as background, which means the goodness of fit applies to the crystalline component. The obtained diffractograms and the standard powder patterns for the zeolite framework types MFI and CHA from *IZA-SC* have been illustrated using *OriginPro*®¹², with the standard powder patterns serving as suitable references.

In addition, scanning electron microscopy imaging was performed on JEOL JSM-6700F field emission scanning electron microscope under an operating voltage of 10 kV. Besides this, X-ray photoelectron spectroscopy was performed for composition analysis by using a Thermo Scientific K α instrument with a monochromated Al K α X-ray source at 1486.6 eV that was operated in constant analyzer energy mode. High resolution and survey spectra were recorded with a respective pass energy of 50 and 200 eV, and a respective binding energy step size of 0.1 and 1.0 eV. Scans were carried out at a spot size of 400 µm. XPS spectra were analyzed via the programs *Thermo Avantage*® and *CasaXPS*®.

Moreover, solid-state nuclear magnetic resonance experiments were carried out on Bruker Avance 300 spectrometer with a widebore 7 T magnet at ambient probe temperature. Using a standard Bruker 4 mm double-resonance

magic-angle spinning probe with powdered samples packed into zirconia rotors of 4 mm in diameter, ¹H, ²⁷Al and ²⁹Si MAS NMR were recorded respectively at 300.1, 78.2 and 59.6 MHz and spun at MAS rates of 12, 12 and 8 kHz with pulse durations of 2, 2 and 1 μ s, recycle delays of 30, 30 and 5 s, acquisition times of 999.9, 20.4 and 42.9 ms, and scans amounting to 8, 511 and 29,090 times. MAS NMR spectra were analyzed via the program *Bruker TopSpin*®. Finally, FTIR spectroscopy was performed on a Bruker Alpha FTIR spectrometer to determine the existence of specific functional groups and to conduct a qualitative assessment of zeolite acidity. Approximately 7 mg of each sample were pressed into a thin pellet, fitted into the KBr window of the FTIR *in situ* cell, and then thermally treated from room temperature to 600°C. Transmission spectra were recorded in steps of 100°C within the range of 4000 to 400 \cdot cm⁻¹.

5.4 Results and Discussion

5.4.1 Powder X-ray Diffraction

Synthesis of SSZ-13@SAPO-34 as a Function of Crystallization Time, and Preparation of Mechanical Mixtures of SSZ-13 with SAPO-34

The calculated cell parameters *a*, *b* and *c*, the goodness of fit, and the LVoI-IB crystallite sizes for previously prepared mechanical mixtures of assynthesised SSZ-13 with commercial SAPO-34 under varying weight ratio of the former, and for SSZ-13 and SSZ-13@SAPO-34 samples are listed in Tables 5.5 and 5.6. It should be noted that the goodness of fit indicates a better Pawley refinement when its value is closer to 1. In addition, the estimated errors or standard deviations in this chapter on the refined cell parameters and LVoI-IB crystallite size from *Topas* have been determined for the CHA phase as $a = b = \pm 0.024$ Å, $c = \pm 0.137$ Å, for the MFI phase as $a = \pm 0.193$ Å, $b = \pm 0.054$ Å, $c = \pm 0.129$ Å, and for the crystallite size as LVoI-IB = ± 83.206 nm. In Table 5.5, the mechanical mixtures of as-synthesised SSZ-13 with commercial SAPO-34 are catalogued according to their weight ratios.

These were prepared to observe in the XRD patterns how the intensity of the diffraction peaks corresponding to SSZ-13 and SAPO-34 shifts with varying weight ratios. For that reason, they should be used as references when comparing with the patterns of the attempted SSZ-13@SAPO-34 materials. From what can be gathered, the mechanical mixtures of SSZ-13 with SAPO-34 feature diffraction peaks not belonging to the CHA phase as the weight ratio of SSZ-13 increases. This is because the as-synthesised SSZ-13 sample used for the mechanical mixtures contains traces of what may be quartz or magadiite according to the Bruker EVA database. However, this should not pose a problem because it allows to create a contrast with the SAPO-34 component of the mixtures. If the as-synthesised SSZ-13 was pure, it would be difficult to monitor how the intensity of the diffraction peaks of SSZ-13 and SAPO-34 evolve with different weight ratios since both components possess the CHA framework. Despite the goodness of fit reaching values up to 4.648 with 0.51 SSZ-13: 1.0 SAPO-34, the diffractograms of the mechanical mixtures are sufficiently crystalline to carry out Pawley refinement. Regarding the cell parameters, a or b tend to decrease with a growing weight ratio of SSZ-13, whereas c does not appear to show any particular trend despite the modified weight ratios. Furthermore, the values of the LVol-IB crystallite size manifest a broad range from 188.12 nm to 2096.0 nm, albeit without an evident trend.

Table 5.5: Targeted and actual zeotype phase, goodness of fit, cell parameters
and crystallite size of mechanical mixtures of SSZ-13 with SAPO-34 calculated
using Pawley refinement.

Sample code	Targeted/actual zeotype phase(s)	Goodness of fit [-]	Cell parameters a, b, c [Å]	LVol-IB crystallite size [nm]
0.06 SSZ-13 : 1.0 SAPO-34	CHA/CHA	1.733	<i>a</i> = <i>b</i> = 13.604, <i>c</i> = 14.911	673.42
0.21 SSZ-13 : 1.0 SAPO-34	CHA/CHA & unknown	3.26	<i>a</i> = <i>b</i> = 13.599, <i>c</i> = 14.911	2096.0
0.36 SSZ-13 : 1.0 SAPO-34	CHA/CHA & unknown	4.069	<i>a</i> = <i>b</i> = 13.589, <i>c</i> = 14.909	1431.8
0.51 SSZ-13 : 1.0 SAPO-34	CHA/CHA & unknown	4.648	<i>a</i> = <i>b</i> = 13.577, <i>c</i> = 14.901	249.17
0.66 SSZ-13 : 1.0 SAPO-34	CHA/CHA & unknown	4.394	<i>a</i> = <i>b</i> = 13.573, <i>c</i> = 14.910	188.12

Table 5.6 portrays the synthesis of SSZ-13 and SSZ-13@SAPO-34 materials as a function of crystallization time. Despite SSZ-13(24h-age/144h) exhibiting additional diffraction peaks not corresponding to the CHA framework, its diffractogram is crystalline enough to attain the goodness of fit, cell parameters and LVol-IB crystallite size. However, the employed approach for

synthesising SSZ-13@SAPO-34 was not successful because all their diffractograms appear amorphous. This may be because SAPO-34 was added to the basic synthesis medium (pH \approx 10.5) of the SSZ-13 gel, leading to the dissolution of its CHA framework.

Table 5.6: Targeted and actual zeotype phase, goodness of fit, cell parameters and crystallite size of SSZ-13 and SSZ-13@SAPO-34 materials calculated using Pawley refinement.

Sample code	Targeted/actual zeotype	Goodness of fit	Cell parameters a, b, c	LVol-IB crystallite size
	phase(s)	[-]	[Å]	[nm]
SSZ-13(24h-age/144h)	CHA/CHA & unknown	8.772	a = b = 13.503, c = 14.903	113.31
SSZ-13@SAPO-34(24h-	CHA/amorphous	-	-	-
age/24h)				
SSZ-13@SAPO-34(24h-	CHA/amorphous	-	-	-
age/48h)				
SSZ-13@SAPO-34(24h-	CHA/amorphous	-	-	-
age/120h)				
SSZ-13@SAPO-34(24h-	CHA/amorphous	_	-	_
age/144h)	onivanopriodo			

Figure 5.1 displays the CHA standard powder pattern as well as diffractograms from the five mechanical mixtures of as-synthesised SSZ-13 with commercial SAPO-34 under variation of the weight ratio of the former. As a reminder, experimental patterns are organized from bottom to top with ascending weight ratio of SSZ-13. Because both SAPO-34 and SSZ-13 possess a CHA framework, the diffractograms essentially overlap with the correspondent diffraction peaks of the CHA reference, e.g. (-1 1 0) and (-2 1 0). This leads effectively to no shift in the intensity of the diffraction peaks of the experimental patterns despite the divergent weight ratios. However, additional peaks not matching with the CHA phase, such as the one at approximately 2 θ = 26.6°, may be due to traces of quartz or magadiite in the as-synthesised SSZ-13.



Figure 5.1: XRD patterns of CHA standard and five mechanical mixtures of assynthesised SSZ-13 with commercial SAPO-34 under variation of the weight ratio of the former. Normalized intensity is plotted against the diffraction angle 2θ .

The standard powder pattern for the CHA framework, as well as the recorded diffractograms for the as-synthesised SSZ-13 sample and four attempted SSZ-13@SAPO-34 materials, are illustrated in Figure 5.2. While SSZ-13(24h-age/144h) emerges as crystalline and overlaps appreciably with the CHA phase, for instance at (1 0 0) and (2 1 1), other diffraction peaks belonging possibly to quartz or magadiite crop up as well, such as the ones near 2 θ = 6° and 27°. Regarding the attempted SSZ-13@SAPO-34 materials, they only differ in their crystallization time. It can be recognized that they consist basically of only amorphous material, and therefore do not match with the CHA reference. The strong basic synthesis medium (pH \approx 10.5) is likely responsible for the disintegration of the CHA zeotype framework of the core material.



Figure 5.2: XRD patterns of CHA standard, as-synthesised SSZ-13, and four samples targeting SSZ-13@SAPO-34 materials following 24 h, 48 h, 120 h and 144 h crystallization. Normalized intensity is plotted against the diffraction angle 2 θ .

Synthesis of Silicalite-1@SSZ-13 as a Function of Crystallization Time and Hydrolysis Condensation

Here, the calculated cell parameters *a*, *b* and *c*, the goodness of fit, and the LVoI-IB crystallite sizes for previously as-synthesised SSZ-13 and silicalite-1@SSZ-13 samples are listed in Table 5.7. In addition, a selection of the diffraction patterns after Pawley refinement is available in the Appendices (see Chapter 7.1, Figures 7.7, 7.8 and 7.9). It should be noted that the goodness of fit indicates a better Pawley refinement when its value is closer to 1. As can be gathered from Table 5.7, the synthesis of silicalite-1@SSZ-13 materials has been attempted under the influence of different crystallization times by way of hydrolysis condensation of TEOS with acetic acid. The sample code tag "SiO₂" corresponds to a reference sample which denotes that TEOS in the respective

reactant gel was converted to amorphous SiO₂ through hydrolysis condensation with AcOH, but with no further attempt of amorphous SiO₂ being converted to silicalite-1. From what can be observed, all the attempted silicalite-1@SSZ-13 materials emerge as considerably crystalline. In the case of SSZ-13(KH)/c650 and SiO₂@SSZ-13(AcOH), these feature a CHA framework with a notably high crystallinity. In addition, the values of goodness of fit are highly satisfactory for all the samples, with the highest value standing at 3.195 for Silicalite-1@SSZ-13(144h/AcOH). Nonetheless, even if the shell@core systems feature CHA and MFI diffraction peaks in their XRD patterns, this does not necessarily mean that MFI@CHA materials are present; a mechanical mixture of the corresponding crystals would also display a similar pattern. With reference to the cell parameters belonging to the CHA and MFI phases of the silicalite-1@SSZ-13 materials, these do not appear to indicate a pattern that depends on the crystallization time. Lastly, the LVol-IB crystallite sizes of the silicalite-1@SSZ-13 samples show an extreme fluctuation between 312.78 nm and 4489.5 nm, possibly caused by limitations from the Pawley refinement; it is interesting to observe that the LVol-IB crystallite size of SiO₂@SSZ-13(AcOH), which is prior to the hydrothermal synthesis of silicalite-1@SSZ-13, is relatively low compared to that of these shell@core materials.

Table 5.7: Targeted and actual zeotype phase, goodness of fit, cell parameters and crystallite size of SSZ-13 with and without condensed SiO₂, and silicalite-1@SSZ-13 materials calculated using Pawley refinement.

Sample code	Targeted/actual zeotype	Goodness of fit	Cell parameters a, b, c [Å]	LVol-IB crystallite size
	phase(s)	[-]		[nm]
SSZ-13(KH)/c650	CHA/CHA	2.426	<i>a</i> = <i>b</i> = 13.562, <i>c</i> = 14.759	122.12
SiO2@SSZ-13(AcOH)	CHA/CHA	2.650	<i>a</i> = <i>b</i> = 13.548, <i>c</i> = 14.761	155.07
Silicalite-1@SSZ- 13(24h/AcOH)	MFI & CHA/MFI & CHA	2.303	a = b = 13.609, c = 14.826 (CHA); a = 20.397, b = 19.684, c = 13.101 (MFI)	4489.5
Silicalite-1@SSZ- 13(48h/AcOH)	MFI & CHA/MFI & CHA	1.611	a = b = 13.593, c = 14.777 (CHA); a = 19.983, b = 19.769, c = 13.378 (MFI)	312.78
Silicalite-1@SSZ- 13(144h/AcOH)	MFI & CHA/MFI & CHA	3.195	a = b = 13.551, c = 15.118 (CHA); a = 19.991, b = 19.815, c = 13.370 (MFI)	4489.5

Together with the CHA and MFI standard powder patterns, Figure 5.3

portrays the experimental diffractograms obtained for a previously assynthesised SSZ-13 sample with and without condensed SiO₂, and for three attempted silicalite-1@SSZ-13 materials subjected to hydrolysis condensation of TEOS with acetic acid during synthesis. Furthermore, the attempted silicalite-1@SSZ-13 materials also experienced different crystallization times, with a descending crystallization time starting from the top pattern. As expected, the rather crystalline samples SiO₂@SSZ-13(AcOH) from hydrolysis condensation and SSZ-13(KH)/c650 do not exhibit any additional diffraction peaks apart from the ones of the CHA phase, e.g. (-1 1 0) and (-2 1 0). Regarding the attempted silicalite-1@SSZ-13 materials, the CHA phase from SSZ-13 appears to gradually lose relative intensity and be replaced by the MFI phase of silicalite-1 with longer crystallization times. It is possible that a recrystallization of SSZ-13 to ZSM-5 has taken place, in other words one conclusion is that the CHA framework topology of SSZ-13 has dissolved and given way to the MFI type. Finally, the diffractograms feature flatter baselines with extended crystallization periods and thus greater crystallinity that is evident with the diffraction peaks from the MFI phase, e.g. (1 0 1) and (5 0 1).



Figure 5.3: XRD patterns of CHA and MFI standards, previously as-synthesised SSZ-13 sample with and without condensed SiO₂, and three samples targeting silicalite-1@SSZ-13 materials after hydrolysis condensation following 24 h, 48 h and 144 h crystallization. Normalized intensity is plotted against the diffraction angle 2 θ .

Recrystallization of SSZ-13 (CHA) to ZSM-5 (MFI) as a Function of Recrystallization Time and Hydrolysis Condensation

Last but not least, the calculated cell parameters *a*, *b* and *c*, the goodness of fit, and the LVoI-IB crystallite sizes for commercial SSZ-13 and attempted ZSM-5 samples are listed in Table 5.8. It should be noted that the goodness of fit indicates a better Pawley refinement when its value is closer to 1. In Table 5.8, the recrystallization products of SSZ-13 to ZSM-5 are catalogued as a function of crystallization time and whether hydrolysis condensation was employed. The sample code tag "AcOH" indicates that hydrolysis condensation of TEOS with acetic acid was performed as an intermediary step for the recrystallization of SSZ-13 to ZSM-5. It should be

highlighted that out of the recrystallization products which did not include condensed SiO₂ in the preparation procedure, only ZSM-5(SSZ-13recryst. 144h) had enough yield during product recovery that could be analysed; the remaining had disintegrated in the product solution. From what can be observed, only two of the recrystallization products emerge as considerably crystalline following 144 h of recrystallization. Moreover, they only display a CHA phase, suggesting that no recrystallization to ZSM-5 occurred and that the products are actually SSZ-13 from before the recrystallization. In the case of the commercial sample SSZ-13(com.), it features a CHA framework with a notably high crystallinity. In addition, the values of goodness of fit are highly satisfactory for the three crystalline samples, with the highest value standing at 3.476 for SSZ-13(com.). With reference to the cell parameters belonging to the CHA phase of the three crystalline materials, these do not appear to indicate a pattern that depends on the crystallization time or hydrolysis condensation. Lastly, the LVol-IB crystallite sizes of the recrystallization samples after 144 h show a large discrepancy, with ZSM-5(SSZ-13-recryst. 144h) at 1369.3 nm and ZSM-5(SSZ-13-recryst. 144h/AcOH) at 341.17 nm; the absence or presence of condensed SiO₂ during recrystallization may be triggering this difference. It is also striking that the LVol-IB crystallite size of SSZ-13(com.), which is prior to the attempted recrystallization to ZSM-5, is appreciably low compared to that of these two recrystallization products.

Sample code	Targeted/actual zeotype	Goodness of fit	Cell parameters a, b, c	LVol-IB crystallite size
	phase(s)	[-]	[Å]	[nm]
SSZ-13(com.)	CHA/CHA	3.476	a = b = 13.578, c = 14.801	90.890
ZSM-5(SSZ-13-recryst. 24h)	MFI/amorphous	-	-	-
ZSM-5(SSZ-13-recryst. 48h)	MFI/amorphous	-	-	-
ZSM-5(SSZ-13-recryst. 144h)	MFI/CHA	3.196	<i>a</i> = <i>b</i> = 13.614, <i>c</i> =	1369.3
			14.801	
ZSM-5(SSZ-13-	MFI/amorphous	-	-	-
recryst. 24h/AcOH)				
ZSM-5(SSZ-13-	MFI/amorphous	-	-	-
recryst. 48h/AcOH)				
ZSM-5(SSZ-13-	MFI/CHA	2 024	<i>a</i> = <i>b</i> = 13.601, <i>c</i> =	3/1 17
recryst. 144h/AcOH)		2.324	14.793	341.17

Table 5.8: Targeted and actual zeotype phase, goodness of fit, cell parameters and crystallite size of SSZ-13 and its recrystallization products calculated using Pawley refinement.

The standard powder pattern for the CHA and MFI zeotype frameworks, as well as the recorded diffractograms for commercial SSZ-13 and four samples targeting recrystallization of SSZ-13 to ZSM-5 with and without hydrolysis condensation can be observed in Figure 5.4. Moreover, the attempted recrystallization products were subjected to different crystallization times. According to expectation, the commercial sample SSZ-13(com.) is very crystalline and features only diffraction peaks from the CHA phase, e.g. (-1 1 0) and (-210). Judging by the experimental patterns of the recrystallization samples, none were able recrystallize to ZSM-5 and achieve an MFI phase, e.g. (1 0 1) and (5 0 1). In fact, only ZSM-5(SSZ-13-recryst. 144h) and ZSM-5(SSZ-13-recryst. 144h/AcOH) manifest strong crystallinity and a low baseline, but in the form of a CHA phase. Even though ZSM-5(SSZ-13-recryst. 24h/AcOH) and ZSM-5(SSZ-13-recryst. 48h/AcOH) are essentially amorphous, diffraction peaks corresponding to a CHA framework can be noticed. Despite recrystallization to ZSM-5 not being successful, it appears to be that SSZ-13 is first dissolved in the initial phases of recrystallization and its CHA framework topology is later restored after protracted crystallization times. This also applies to the absence of condensed SiO₂ during recrystallization since no yields were obtained from samples with a lower crystallization time than that of ZSM-5(SSZ-13recryst. 144h).



Figure 5.4: XRD patterns of CHA and MFI standards, commercial SSZ-13, and four samples targeting recrystallization of SSZ-13 to ZSM-5 with and without hydrolysis condensation following 24 h, 48 h and 144 h crystallization. Normalized intensity is plotted against the diffraction angle 2 θ .

5.4.2 Scanning Electron Microscopy

Comparison between As-Synthesised SSZ-13 and Commercial SSZ-13

At a resolution of 1 µm, SEM images were recorded on as-synthesised SSZ-13(24h-age/144h) and commercial SSZ-13. A selection of these images is displayed in Figure 5.5. In the case of SSZ-13(24h-age/144h), its particles can be observed in images [a] and [b] being between 2 and 5 µm in length. Despite there also being amorphous material and other irregular polygonal crystals that may correspond to quartz or magadiite, there is direct evidence of SSZ-13 particles exhibiting its typical cubic morphology¹⁷⁶. As for SSZ-13(com.), it is portrayed in images [c] and [d]. These feature fractured particles and amorphous material covering what appears to be fragmented cubic crystals of

SSZ-13, with dimensions of up to 8 μ m. All in all, it can be said that SSZ-13 has been synthesised despite the presence of specific impurities.



Figure 5.5: SEM images of as-synthesised SSZ-13(24h-age/144h) [a,b] and of commercial SSZ-13 [c,d].

5.4.3 X-ray Photoelectron Spectroscopy

Comparison between As-Synthesised SSZ-13, Commercial SSZ-13 and As-Synthesised Silicalite-1

X-ray photoelectron spectra were recorded for as-synthesised SSZ-13(24h-age/144h), commercial SSZ-13 and as-synthesised silicalite-1 (24 h crystallization). The surface composition results are available in Figure 5.6, which contains the atomic percentage of the assessed elements. In addition, a selection of the XPS spectra with highlighted element scan ranges is available in the Appendices (see Chapter 7.3, Figure 7.13). It can be gathered that assynthesised silicalite-1 possesses the highest value of the atomic percentage for Si, which amounts expectedly to about half of the atomic percentage for O. On the other hand, XPS analysis surprisingly did not yield any feasible value for Al in the case of SSZ-13(24h-age/144h), which suggests at first that there was no or barely any incorporation of Al into the SSZ-13 framework during hydrothermal synthesis. However, since the atomic percentage of O is somewhat larger than double that of Si, it may be that the atomic percentage of Al is too negligible to be detected by *CasaXPS*®. To support this argument, SSZ-13(com.) exhibits values for Si and O and thus a ratio that are nearly identical to those of SSZ-13(24h-age/144h). Because analysis of commercial SSZ-13 also did not deliver a value for Al, it can be assumed that the analysis software could not identify it and that hydrothermal synthesis of SSZ-13 was achieved following the procedure of SSZ-13(24h-age/144h).



Figure 5.6: Atomic percentage of the XPS assessed elements (Si, O) for assynthesised SSZ-13(24h-age/144h), commercial SSZ-13 and as-synthesised silicalite-1 (24 h crystallization).

5.4.4 Solid-state Nuclear Magnetic Resonance Spectroscopy

Solid-state NMR of Commercial SSZ-13

Solid-state ¹H, ²⁷Al and ²⁹Si MAS NMR spectra were recorded for commercial SSZ-13 to have a reference on the characteristic signals that describe the environment of these elements in the structure of this class of material. Its ¹H MAS NMR spectrum can be observed in Figure 5.7. The signal corresponding to bridging hydroxyls in Si-OH-Al groups (Brønsted acid sites) appears to be low-field-shifted to 6.55 ppm¹⁷⁷. Furthermore, signal broadening suggests that these sites are hydrated.



Figure 5.7: ¹H MAS NMR spectrum of commercial SSZ-13.

Figure 5.8 portrays the ²⁷AI MAS NMR spectrum of commercial SSZ-13. The resonance with the chemical shift at 54.10 ppm results from the existence of tetrahedrally coordinated AI atoms in the framework of the zeolite, whereas the wide peak at -3.68 ppm can be attributed to non-framework aluminium¹⁷⁸.



Figure 5.8: ²⁷AI MAS NMR spectrum of commercial SSZ-13.

The ²⁹Si MAS NMR spectrum with deconvolution results of commercial SSZ-13 is available in Figure 5.9. The corresponding peaks which describe the environment of the SiO₄ tetrahedra in the framework of SSZ-13, namely Si(4AI), Si(3AI), Si(2AI), Si(1AI) and Si(0AI), can be found respectively at -90.69, -95.14,

-99.84, -104.96 and -111.05 ppm and possess relative areas which amount to 3.63%, 5.98%, 14.25%, 32.51% and 43.63%¹⁷⁸. Nevertheless, it should be pointed that the chemical shift of these signals may be slightly displaced towards the low field due to hydration.



Figure 5.9: ²⁹Si MAS NMR spectrum with deconvolution results of commercial SSZ-13.

5.4.5 Infrared Spectroscopy

FTIR Spectroscopy of Commercial SSZ-13

FTIR spectra of commercial SSZ-13, which are illustrated in Figure 5.10, were recorded at different temperatures to observe Brønsted acid sites and specific functional groups related to the framework, as well as to have a reference on this class of material. IR bands located at distinct wavelength regions act as unique identifiers which allow a qualitative assessment of zeolite acidity and the recognition of these functional groups. To start with, the IR band in the region around $3589 \cdot \text{cm}^{-1}$ can be ascribed to bridging Si-OH-AI groups. Nevertheless, it remains hidden at room temperature because of moisture and only becomes more visible with increasing temperatures following dehydration¹⁷⁹. This situation reverts after the sample pellet is cooled down to 50°C. What is more, the band at $1626 \cdot \text{cm}^{-1}$ at room temperature further

supports the existence of adsorbed water, which slowly disappears with the *in situ* thermal treatment. Regarding the functional groups of the SSZ-13 framework, the IR band at around $462 \cdot \text{cm}^{-1}$ reveals the presence of T-O bends originating from SiO₄ and AlO₄ framework tetrahedra. Double rings vibration from the secondary building unit of the zeolite can be allocated to the band located at $640 \cdot \text{cm}^{-1}$. In addition, symmetric stretching vibrations of T-O-T groups are inferred from the diminished transmittance at about $740 \cdot \text{cm}^{-1}$. Finally, the band at around $1068 \cdot \text{cm}^{-1}$ can be assigned to asymmetric stretching vibrations of T-O-T groups (T = Al or Si)¹⁷⁸.



Figure 5.10: Transmittance FTIR spectra of commercial SSZ-13 at different temperatures.

5.5 Conclusions and Discussion

Regarding the XRD pattern of as-synthesised SSZ-13(24h-age/144h), it manifests agreeable overlapping with the CHA reference as well as not characteristic peaks which indicate traces of what may be quartz or magadiite. As for the four targeted as-synthesised shell@core materials based on SSZ-

13@SAPO-34, these are essentially amorphous and do not match with the CHA reference. The disintegration of the CHA framework in the core appears to have been induced by the very basic synthesis medium.

Judging from the XRD patterns of the attempted silicalite-1@SSZ-13 materials, all emerge as considerably crystalline. Hydrothermal synthesis of these samples was carried out after hydrolysis condensation of TEOS with acetic acid, suggesting that this method has allowed to maintain the SSZ-13 framework essentially intact during synthesis. Nonetheless, the fact that there are CHA and MFI diffraction peaks in the XRD patterns does not necessarily imply that MFI@CHA materials are present. Synthesis of silicalite-1@SSZ-13 materials has not necessarily been achieved due to the fact that a mechanical mixture of the corresponding crystals would also result in a similar pattern. Apart from this, the MFI phase of SSZ-13 with more protracted crystallization times. It may also be that a recrystallization from the CHA framework topology of SSZ-13 to the MFI type of ZSM-5 is occurring. Finally, the diffractograms exhibit flatter baselines with longer crystallization peaks of the MFI phase.

Concerning the recrystallization of SSZ-13 to ZSM-5 with and without hydrolysis condensation, none were able to recrystallize to ZSM-5 and generate an MFI phase. In fact, only those following 144 h of recrystallization emerge as considerably crystalline. Nevertheless, they only possess a CHA phase, indicating that the products are actually SSZ-13 from before the recrystallization. Recrystallization periods shorter than 144 h deliver either no yield or essentially amorphous products. Even though recrystallization to ZSM-5 was not achieved, it can be concluded that SSZ-13 is dissolved in the first stages of recrystallization and its CHA framework topology is later reconstituted after extended crystallization times.

Regarding the SEM images, as-synthesised SSZ-13(24h-age/144h) shows evidence of SSZ-13 particles with cubic morphology despite there also being amorphous material and other irregular polygonal crystals which may belong to magadiite or quartz. Moreover, fragmented cubic crystals in commercial SSZ-13 further confirm that this class of material was synthesised. Furthermore, XPS spectra were recorded to measure the variation of the atomic

percentages of Si and O for as-synthesised SSZ-13(24h-age/144h), commercial SSZ-13 and as-synthesised silicalite-1 (24 h crystallization). As-synthesised silicalite-1 features the highest value of the atomic percentage for Si, which amounts expectedly to about half of the atomic percentage for O. Surprisingly, an appreciable value for AI was not obtained in the case of SSZ-13(24h-age/144h), implying that there was no or barely any incorporation of AI into the SSZ-13 framework during hydrothermal synthesis. However, the atomic percentage of O is somewhat larger than double that of Si, meaning that the atomic percentage of AI is perhaps too low to be distinguished by the analysis software. Given the fact that analysis of commercial SSZ-13 exhibits values for Si and O nearly identical to those of SSZ-13(24h-age/144h) yet also no value for AI, it seems likely that hydrothermal synthesis of SSZ-13 was achieved via the procedure of SSZ-13(24h-age/144h).

With reference to the solid-state MAS NMR spectra of commercial SSZ-13, the characteristic signals of this class of material can be observed. Nevertheless, the signal broadening in the ¹H MAS NMR spectrum and the slight displacement of the correspondent peaks for Si(4AI), Si(3AI), Si(2AI), Si(1AI) and Si(0AI) from their standard chemical shift in the ²⁹Si MAS NMR spectrum suggests that the sample is hydrated. Finally, the FTIR spectra of commercial SSZ-13 show bands originating from T-O bends, double rings vibration from the secondary building unit, symmetric stretching vibrations of T-O-T groups and asymmetric stretching vibrations of T-O-T groups (T = AI or Si). In the case of hydroxyl Si-OH-AI groups, these are at first not observable because of hydration. The respective IR band only reveals itself after the *in situ* thermal treatment of SSZ-13. For this reason, the presence of adsorbed water further justifies the abovementioned interpretation of the ¹H and ²⁹Si MAS NMR spectra.

Chapter 6: Conclusions and Future Work

6.1 Conclusions

Variations of gel composition, order of addition of chemicals and nature of extracting final product of SAPO-34, and shell@core type synthesis methods involving SAPO-34, SSZ-13, and silicalite-1 were investigated in this thesis to understand the underlying gel chemistry and establish a connection with structural properties. In chapter three, SAPO-34 synthesis methods and its gel chemistry were explored to improve directed incorporation of silicon into the zeolite framework as well as achieve greater stability. Via structural characterisation techniques, it was possible to detect a correlation with the structural properties of SAPO nanoporous systems.

Based on the XRD patterns of the SAPO-34 samples with a target gel composition of 2 mol% Si, the liquid phase centrifugates exhibits the greatest phase purity and a higher relative crystallinity given the low baseline. In addition, most SAPO-34 samples that were generated from a reaction gel with 10 mol% Si manifest high crystallinity in the recorded diffractograms and fit satisfactorily with the CHA standard powder pattern. On the other hand, those produced from 25 mol% Si in the reaction gel show an elevated content of amorphous material and thus feature an uneven baseline. After performing calcination runs on processing-dependent as-synthesised SAPO-34 samples, it has established that 190116[A] {...} spc/c900 been and 190116[A] {...} lpc/c900 (both from precipitated SiO₂ with 10 mol% Si in the reaction gel, following the order of addition 1 during synthesis) are the only samples which kept their CHA framework relatively intact. Regarding the solidstate MAS NMR spectra, the two aforementioned samples possess the characteristic signals of SAPO-34 despite evidence of hydration. Apart from SEM revealing the cubic-like rhombohedral morphology of the SAPO-34 crystals, EDS spectra also confirm the availability of Si, Al, P and O, implying that silicoaluminophosphates are present. Lastly, the FTIR spectra of commercial and as-synthesised SAPO-34 show bands stemming from T-O bends, D6R rings, symmetric stretching of P-O or AI-O groups and asymmetric

stretching of O-P-O groups. In the case of hydroxyl Si-OH-Al groups, these only reveal themselves after the *in situ* thermal treatment of SAPO-34.

In chapter four, shell@core synthesis variations for silicalite-1@SAPO-34 compositions were studied to gain a better understanding of the gel chemistry that is involved and enhance the stability of these structures. For this reason, modification of the surface structure of SAPO-34 was targeted by growing a continuous hydrophobic silicalite-1 shell over SAPO-34 core crystals which shields the core from water during SCR while preserving its desired properties. Structural characterisation techniques were utilised to elucidate how different gel chemistry parameters influence the formation of shell@core type nanoporous systems.

It can be inferred from the XRD patterns that the synthesis of samples containing the MFI and CHA frameworks was successful where the approach of pre-treating the SAPO-34 crystals with TPABr followed by pre-crystallization was performed. Ion exchange with TPABr as reported by Razavian and Fatemi may have shielded the SAPO-34 seed crystals from the particularly basic synthesis media of the pre-crystallization silicalite-1 slurry⁷². Regarding the calcined analogous samples, these manage to preserve both framework topologies. In contrast to the aforementioned silicalite-1@SAPO-34 materials, synthesis of silicalite-1@SAPO-34 materials without pre-crystallization culminated in amorphous patterns and therefore no overlapping with the CHA and MFI references. This is irrespective of the fact whether the SAPO-34 crystals were pre-treated with TPABr or not.

An alternative synthesis strategy for silicalite-1@SAPO-34 materials was carried out by means of hydrolysis condensation of TEOS with acetic acid as an intermediary step prior to hydrothermal synthesis. The CHA framework topology in these products matches with the CHA standard (e.g. SAPO-34 and AIPO-34) from *IZA-SC* and appears not to have disintegrated based on the respective XRD patterns¹². One possible reason for this is that amorphous SiO₂ from condensation of TEOS has accumulated on the surface of SAPO-34 crystals and insulated these from the highly basic synthesis medium (pH ≈ 14) of the final reactant gel. Despite the fact that diffraction peaks belonging to an MFI phase are not discernible, a minimal amount of silicalite-1 may have still been generated which does not manifest itself on the experimental patterns due to its

extremely low weight ratio. According to Razavian and Fatemi, the relative intensity of the diffraction peaks corresponding to the two phases in the binary composite is determined by their mass ratios as a result of the shielding effect of materials around core seeds⁷². Apart from this, the intensity of the diffraction peaks relative to the baseline does not seem to shift considerably despite the varied crystallization time.

However, XRD on its own is not enough evidence for the existence of shell@core assemblies. By including SEM images and XPS spectra, the formation of silicalite-1@SAPO-34 materials can be verified. Concerning the SEM images, the characteristic morphology of silicalite-1 is not easily discernible in the attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-Silicalite-1@SAPO-34(48h/AcOH) and Silicalite-1@SAPO-34(24h/AcOH), 34(144h/AcOH). Nevertheless, there seems to be a greater volume of fibrous overgrowth on seemingly fragmented SAPO-34 crystals which correlates with longer crystallization times. As for the SAPO-34 crystals, they do not exhibit an intact cubic-like rhombohedral morphology. For this reason, it is not possible to affirm that silicalite-1@SAPO-34 materials have been formed. After Cu(II) ion exchange, EDS spectra of commercial SAPO-34 and the three attempted silicalite-1@SAPO-34 samples generated from hydrolysis condensation of TEOS with acetic acid corroborate the existence of Si, Al, P, O and Cu, suggesting the incorporation of Cu in the SAPO-34 phase framework.

XPS reveals the variation of the atomic percentages of Si, Al, P and O for commercial SAPO-34 and for the attempted silicalite-1@SAPO-34 samples Silicalite-1@SAPO-34(24h/AcOH), Silicalite-1@SAPO-34(48h/AcOH) and Silicalite-1@SAPO-34(144h/AcOH). Commercial SAPO-34 possesses the lowest atomic percentage for Si, and the highest atomic percentages for Al and P among the analysed samples. Concerning the attempted silicalite-1@SAPO-34 samples, their values for Al and P decline with protracted crystallization times. The values of these two elements should be converging towards zero in the presence of ideal silicalite-1@SAPO-34 materials. As a result, it remains to be seen whether partial silicalite-1@SAPO-34 materials have been synthesised. Following Cu(II) ion exchange, UV-Vis spectra of commercial SAPO-34 and three silicalite-1@SAPO-34 samples derived from hydrolysis condensation of TEOS with acetic acid attest the incorporation of Cu²⁺ ions in the Brønsted acid

sites of the SAPO-34 phase framework even with a silicalite-1 shell around the core.

In chapter five, shell@core synthesis variations for compositions involving SSZ-13, an aluminosilicate material that is isostructural to the SAPO-34 zeolite and used also in SCR and MTO catalysis, were explored to unravel the gel chemistry behind these structures and improve their stability. For this reason, the aim was to modify the surface structure of SSZ-13 by growing a continuous hydrophobic silicalite-1 shell over SSZ-13 core crystals which protects the core from water during SCR while maintaining the desired properties. Laboratory-based characterisation techniques were employed to assess how factors from the gel chemistry affect the synthesis of shell@core type nanoporous systems.

Based on the XRD patterns of the attempted silicalite-1@SSZ-13 materials, all appear to be remarkably crystalline. For these products, hydrolysis condensation of TEOS with acetic acid was performed before proceeding with their hydrothermal synthesis. One conceivable conclusion is that the SSZ-13 framework is protected from the very basic synthesis medium of the reactant gel via this route. However, the coexistence of CHA and MFI diffraction peaks in the XRD patterns does not automatically mean that MFI@CHA materials have been formed; a similar pattern would also be obtained with a mechanical mixture of the corresponding crystals. Even though the diffraction peaks of both phases in the composites are not as strong as those of the CHA (e.g. SSZ-13, SAPO-34 and AIPO-34) and MFI (e.g. silicalite-1 and ZSM-5) standards from IZA-SC, it can be confirmed that they overlap with the reference patterns¹². Besides this, the CHA phase of SSZ-13 seems to be replaced gradually by the MFI phase of silicalite-1 with longer crystallization times. As indicated by Razavian and Fatemi, the shifting mass ratio of the two phases in binary composites has an impact on the relative intensity of the diffraction peaks associated with the two components⁷². In this case, it is possible that the CHA framework topology of SSZ-13 is undergoing recrystallization to the MFI type of ZSM-5. In addition, the diffractograms feature flatter baselines with extended crystallization periods and thus greater crystallinity which can be recognised from the diffraction peaks of the MFI phase. Regarding the recrystallization of SSZ-13 to ZSM-5 with and without hydrolysis condensation, none of the attempts led to the formation of

ZSM-5 and therefore an MFI phase. In spite of the fact that recrystallization to ZSM-5 was not achieved, it can be deduced that dissolution of SSZ-13 takes place in the first stages of recrystallization, followed by the reconstitution of the CHA framework topology after protracted crystallization times.

Concerning the SEM images, as-synthesised SSZ-13(24h-age/144h) features SSZ-13 particles with cubic morphology as well as amorphous material and other irregular polygonal crystals which may be attributed to magadiite or quartz. Even so, the observation of fragmented cubic crystals in commercial SSZ-13 confirm the synthesis of this class of material. Furthermore, XPS was performed to study the variation of the atomic percentages of Si and O for as-synthesised SSZ-13(24h-age/144h), commercial SSZ-13 and as-synthesised silicalite-1 (24 h crystallization). As-synthesised silicalite-1 possesses the highest atomic percentage for Si, which is expectedly equivalent to about half of the value for O. Since the analysis of commercial SSZ-13(24h-age/144h) as well as no value for AI, it seems likely that SSZ-13 was attained following the hydrothermal synthesis procedure of SSZ-13(24h-age/144h).

With reference to the solid-state MAS NMR spectra of commercial SSZ-13, the characteristic signals of this class of material can be observed despite evidence of hydration. Last but not least, the FTIR spectra of commercial SSZ-13 feature bands resulting from T-O bends, double rings vibration from the secondary building unit, symmetric stretching vibrations of T-O-T groups and asymmetric stretching vibrations of T-O-T groups (T = AI or Si). As for the hydroxyl Si-OH-AI groups, these are only discernible after the *in situ* thermal treatment of SSZ-13.

6.2 Future Work

Regarding future work, it would be of interest to assess alternative aluminosilicate and CHA zeolites as seed crystals for synthesis of shell@core materials, as well as vary ageing time and the core crystal mass per reactant gel volume. Moreover, determining further optimal shell@core synthesis conditions is crucial. Because of the substantial difference in the pH value of the

reactant gels for the core and shell zeolites, it is important to find suitable pretreatment methods for the core crystals so that these are better preserved in the synthesis medium and the formation of the composite is facilitated. Besides this, it would be helpful to establish how promoter metal cations (Zn²⁺, Mg²⁺, etc.) affect zeolite framework outcome.

Further characterisation techniques should also be included. Raman spectroscopy should be incorporated to identify the vibration bands of Raman active functional groups. Moreover, zeta potential and ICP-OES measurements would be helpful to establish respectively the electric potential relative to the sample surface as well as the bulk elemental composition of the compounds. For shell@core formation, another alternative is performing atomic layer depositon (ALD) of amorphous silica on the surface of ion-exchanged SAPO-34 seed crystals, followed by crystallization with the template TPAOH. Finally, silicalite-1@Cu/SAPO-34 materials may need to be optimised with the help of stability tests.

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Appendices

7.1 Pawley Refinement of Powder X-Ray Diffraction Patterns



Figure 7.1: Pawley refinement of XRD pattern of the processing-dependent assynthesised SAPO-34 sample 190116[A]_{...}_spc (derived from precipitated SiO₂ with 10 mol% Si in reaction gel, order of addition 1).



Figure 7.2: Pawley refinement of XRD pattern of the processing-dependent assynthesised SAPO-34 sample $190116[A]_{\dots}$ [pc (derived from precipitated SiO₂ with 10 mol% Si in reaction gel, order of addition 1).



Figure 7.3: Pawley refinement of XRD pattern of the processing-dependent assynthesised SAPO-34 sample 190116[B]_{...}_fc (derived from precipitated SiO₂ with 10 mol% Si in reaction gel, order of addition 1).



Figure 7.4: Pawley refinement of XRD pattern of silicalite-1@SAPO-34 sample following 24 h crystallization (with hydrolysis condensation of TEOS with AcOH as an intermediary step and without iPrOH in reactant gel).



Figure 7.5: Pawley refinement of XRD pattern of silicalite-1@SAPO-34 sample following 48 h crystallization (with hydrolysis condensation of TEOS with AcOH as an intermediary step and without iPrOH in reactant gel).



Figure 7.6: Pawley refinement of XRD pattern of silicalite-1@SAPO-34 sample following 144 h crystallization (with hydrolysis condensation of TEOS with AcOH as an intermediary step and without iPrOH in reactant gel).



Figure 7.7: Pawley refinement of XRD pattern of silicalite-1@SSZ-13 sample following 24 h crystallization (with hydrolysis condensation of TEOS with AcOH as an intermediary step).



Figure 7.8: Pawley refinement of XRD pattern of silicalite-1@SSZ-13 sample following 48 h crystallization (with hydrolysis condensation of TEOS with AcOH as an intermediary step).



Figure 7.9: Pawley refinement of XRD pattern of silicalite-1@SSZ-13 sample following 144 h crystallization (with hydrolysis condensation of TEOS with AcOH as an intermediary step).

7.2 Elemental Mapping with Energy-Dispersive X-ray Spectroscopy





Figure 7.10: EDS spectrum coupled with SEM image of Cu(II) ion-exchanged commercial SAPO-34 [a,g], including elemental mapping of Si [b], Al [c], P [d], O [e] and Cu [f].

7.3 Element Scan Ranges in X-ray Photoelectron Spectroscopy





Figure 7.11: Survey XPS spectrum [a] of commercial SAPO-34, including highlighted element scan ranges of Si [b], AI [c], P [d] and O [e].



Figure 7.12: Survey XPS spectrum [a] of silicalite-1@SAPO-34 sample following 144 h crystallization (with hydrolysis condensation of TEOS with AcOH as an intermediary step and without iPrOH in reactant gel), including highlighted element scan ranges of Si [b], AI [c], P [d] and O [e].



Figure 7.13: Survey XPS spectrum [a] of commercial SSZ-13, including highlighted element scan ranges of Si [b] and O [c].