MICROWAVE INDUCED SOLID-STATE INTERACTIONS FOR THE SYNTHESIS OF FISCHER-TROPSCH CATALYSTS

Linda Zikhona Linganiso

A thesis submitted to the faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy.

Johannesburg, 2008

Dedicated to: Almighty God

DECLARATION

I hereby declare that microwave induced solid-state interactions for the synthesis of Fischer-Tropsch Catalysts is my own work and is submitted to the University of the Witwatersrand for the degree of Doctor of Philosophy and has not been previously submitted for any other degree in any other university and all the material contained herein has been acknowledged.

.....

Linda Zikhona Linganiso

.....day of Month 2008

ACKNOWLEDGEMENTS

My heartfelt gratitude goes out to the following people:

- [1] Almighty God for being my source of strength, helper and the internal motivator.
- [2] Prof. Mike S. Scurrell, my supervisor for his valuable guidance throughout my research. I would love to thank him for his encouragement and the ability he has to instruct me during hard times of this project.
- [3] Prof. Neil J. Coville for co-supervising me when Prof. Mike was not feeling well.
- [4] Prof. Michael Claeys and Prof. Eric van Steen, for giving me the opportunity to do some experiments at University of Cape Town (UCT) and for supervising as well.
- [5] Basil Chassoulas and physics workshop guys for the moral and technical support.
- [6] My friend Itai Evans Mabaso for his valuable assistance, inputs and the fruitful discussions we have had together.
- [7] Ademola Rabiu for his support and advice towards this work.
- [8] Kalala Jalama for the inputs he has given towards this thesis.
- [9] Thanks to all my CATOMMAT friends for their help and a friendly environment to work.
- [10] My friend Alex Kamunyu for his valuable support, proof reading and editing of this thesis.
- [11] NRF Centre of Excellence in Catalysis, Canon Colin's Educational Trust of South Africa and South African National Energy Research Institute (Saneri) for financial assistance.
- [12] Special thanks to the University of the Witwatersrand, department of Chemistry for affording me the opportunity to carry out this research. I would like to thank the Chemistry staff members and the fellow post graduates for being useful, kind and for creating extremely nice environment to work.

[13] But I simply have to mention my family, Mandlovu, Phumzile, Minki, Unathi, Ella, Loloza, Inathi and Sikelelwe) for the support they always give me throughout my studies.

PUBLICATIONS AND PRESENTATIONS ARISING FROM THIS WORK

Presentations

- CATSA 2006: Poster presentation : "Microwave effect on Fischer-Tropsch synthesis"
- CATSA 2007: Oral presentation: "Microwave effect on Fischer-Tropsch synthesis"
- CATSA 2008: Poster presentation: "Effect of the power level on catalytic activity and selectivity on Fischer-Tropsch synthesis".

Publications

- Patent: "Improvement in the efficiency of Catalysts" submitted.
- 2008: "Microwave effect on Fischer-Troscph synthesis" to be submitted.
- 2008: "Microwave radiation-induced solid-state modification and improved selectivities of iron Fischer-Tropsch catalysts" to be submitted.

NOMENCLATURE

LIST OF ABBREVIATIONS

ASF	Anderson-Schultz-Flory
BET	Brunauer-Emmett-Teller
BT	Barium titanate
CS	Conventional sintered
CSTR	Continuous stirred tank reactor
FID	Flame ionization detector
FTS	Fischer-Tropsch synthesis
FT	Fischer-Tropsch
GC	Gas chromatography
HCNs	Hydrocarbons
HTFT	High temperature Fischer-Tropsch
IWI	Incipient wetness impregnation
LTFT	Low temperature Fischer-Tropsch
MS	Microwave sintered
PIC	Pressure indicator control
PXRD	Powder X-Ray diffraction
SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TIC	Temperature indicator control
TGA	Thermogravimetric analysis
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
TPSR	Temperature programmed surface reaction
RT	Room temperature
μλ	Microwave
Vent	Ventilation

WGS Water gas shift reaction

NOTATION

- GHSV Gas Hourly Space Velocity
- TOF Turnover frequency

TABLE OF CONTENTS

Declaration	iii
Acknowledgements	iv
Nomenclature	vii
Table of contents	ix
List of figures	xviii
List of tables	XXX
Abstract	xxxii
Chapter 1 Introduction	1
1.1 History and development	1
1.2 Effect of crystallite size on activity and selectivity of Fischer-Tropsch	
catalysts	3
1.3 Iron catalyst and potassium as a promoter	4
Chapter 2 Fischer-Tropsch synthesis	6
2.1 The Fischer-Tropsch synthesis (FTS)	6
2.1.1 The Fischer-Tropsch reactions	8
2.2 Fischer-Tropsch reaction mechanisms	10
2.2.1 Introduction	10
2.2.2 Alkyl mechanism	11
2.2.3 Alkenyl mechanism	13
2.2.4 Oxygenate (enol) mechanism	14
2.2.5 CO insertion mechanism	15

2.2.6 Formation of branched hydrocarbons	16
2.3 The Fischer-Tropsch product spectrum	17
2.4 Effect of reaction and reactor variables on the product	
selectivity	
2.4.1 Choice of reactor	18
2.4.2 Operating conditions	19
2.4.2.1 Total pressure	19
2.4.2.2 Reaction temperature	20
2.4.2.3 H ₂ : CO ratio	21
2.4.2.4 The nature of the catalyst	21
2.5 The Fischer-Tropsch catalysts	
2.5.1 Introduction	22
2.5.2 Iron	22
2.5.3 Cobalt	23
2.5.4 Ruthenium	23
2.5.5 Nickel	24
2.5.6 Other Fischer-Tropsch catalysts	24
2.5.7 Promoters	25
2.5.7.1 Chemical promoters	25
2.5.7.1.1 Potassium	26
2.5.7.1.2 Effect of over-promoting iron catalyst with	
Potassium	27
2.5.7.1.3 Effect of promoting iron catalyst with	

potassium on the water-gas shift reaction	30	
2.5.7.2 Reduction promoters	30	
2.5.7.2.1 Copper	30	
2.5.7.3 Structural promoter or supports	31	
2.5.7.3.1 Silica (SiO ₂)	33	
2.6 Changes within the catalyst during FT synthesis	34	
2.6.1 Phase changes	34	
2.6.2 Iron phase	34	
2.6.3 Catalyst deactivation	35	
2.6.3.1 Introduction	35	
2.6.3.2 Poisoning	36	
2.6.3.3 Fouling	37	
2.6.3.4 Sintering	38	
2.7 Effect of temperature pre-treatment (calcination) of the catalyst on the		
performance of the catalyst	39	
2.8 Methods of catalyst preparation	42	
2.8.1 Introduction	42	
2.8.2 Supported catalysts	43	
2.8.2.1 Preparation of supported FT catalysts	44	
2.8.2.1.1 Precipitation method	44	
2.8.2.1.2 Impregnation method	44	

3.1 Introduction	46
3.2 Microwave effect in the synthesis and sintering of solid materials	47
3.3 Microwave effect in catalysis	48
3.4 How does microwave irradiation provide heating	52
3.5 The expected benefits of microwave heating on Fischer-Tropsch synthesis	53
Chapter 4 Scope of this study	54
Chapter 5 Experimental methods	56
5.1 Catalyst preparation	56
5.1.1 Preparation of unsupported iron catalysts	56
5.1.2 Preparation of supported iron catalysts	57
5.1.3 Preparation of supported cobalt catalyst	58
5.1.4 Microwave pre-treatment of the iron catalysts	58
5.2 Reagents	58
5.3 Catalyst characterization	59
5.3.1 Introduction	59
5.3.2 Thermogravimetric analysts (TGA)	59
5.3.3 Powder X-ray diffraction	60
5.3.4 Temperature programmed reduction	60
5.3.5 Brunauer-Emmett-Teller (BET) method	60
5.3.6 Transmission electron microscopy (TEM)	61
5.3.7 X-ray florescence (XRF) spectroscopy	61

5.3.8 Scanning electron microscopy (SEM)	61
5.3.9 Transmission Möosbauer spectroscopy	62
5.3.10 Centrifuge	62
5.3.11 Temperature programmed surface reactions (TPSR)	62
5.3.12 TOF- secondary ion mass spectrometry (SIMS)	63
5.4. Fischer-Tropsch reactions	63
5.4.1 Experimental setup	63
5.4.2 Choice of reactor and catalyst packing	66
5.4.3 Experimental procedure	68
5.5 Product analysis	69
5.5.1 Quantification of the products	69
5.5.2 Data analysis	70
5.5.3 Analysis conditions (GC)	71
5.6 Hydrogenation of ethylene	
Chapter 6 Results and Discussion	72
6.1 Introduction	72
6.2 Characterization of unsupported catalysts	73
6.2.1 Microwave effect	73
6.2.1.1 TEM analysis	73
6.2.1.2 PXRD analysis	75
6.2.1.3 Surface area	76
6.2.1.4 H ₂ -TPR analysis	79

6.2.1.5 SEM analysis	80
6.3 Characterization of partially reduced iron catalysts	81
6.3.1 Microwave effect	81
6.3.1.1 TEM analysis	81
6.3.1.2 PXRD analysis	83
6.3.1.3 H ₂ -TPR analysis	85
6.4 Characterization of the Fe/K catalysts	86
6.4.1 Microwave effect	86
6.4.1.1 TEM analysis	86
6.4.1.2 PXRD analysis	88
6.4.1.3 BET analysis	88
6.4.2 Effect of the power level	90
6.4.2.1 TEM analysis	90
6.4.2.2 PXRD analysis	92
6.4.2.3 Surface area	93
6.4.3 Effect of duration	95
6.4.3.1 PXRD analysis	95
6.4.3.2 BET analysis	96
6.4.4 Effect of bed size and shape	98
6.4.4.1 PXRD analysis	98
6.4.4.2 BET analysis	99
6.5 Characterization of supported iron catalysts	100
6.5.1 Thermogravimetric analysis (TGA)	101

6.5.2 Temperature programmed reduction (TPR)	102
6.5.3 PXRD analysis	103
6.5.4 Surface area determination	104
6.5.5 Mössbauer spectroscopy analysis	105
6.5.6 Microwave effect	106
6.5.6.1 H ₂ -TPR analysis of Fe\SiO ₂ catalysts	106
6.5.6.2 Surface area	107
6.5.6.3 PXRD analysis	109
6.5.6.4 Temperature-Programmed surface reactions (TPSR)	110
6.5.6.5 Secondary ion mass spectrometry (SIMS) analysis	112
.6 Summary of the characterization results of iron catalyst and conclusion	113
.7 Fischer-Tropsch synthesis	114
6.7.1 Effect of potassium promotion on Fe/SiO ₂ catalysts	114
6.7.1.1 Catalytic measurements	114
6.7.1.2 Formation of carbon dioxide	116
6.7.1.3 Formation of organic products	117
6.7.1.3.1 Methane formation	118
6.7.1.3.2 Average molecular weight	119
6.7.1.3.3 Olefin formation	121
.8 Effect of microwave pre-treatment on Fe/SiO ₂ catalysts	123
6.8.1 Activity measurements of a calcined Fe/SiO ₂ catalyst	123
6.8.2 Carbon dioxide selectivity	124
6.8.3 Methane selectivity	125

6.8.4 Olefin selectivity	126
6.8.5 Effect of microwave on catalytic activity and selectivity of Fe/SiO_2	
Catalyst precursor (dried at 110°C)	127
6.8.5.1 Carbon monoxide conversion	127
6.8.5.2 Carbon dioxide selectivity	128
6.8.5.3 Methane selectivity	129
6.8.5.4 Olefin selectivity	130
6.8.6 Hydrogenation of ethylene: activity measurements	131
6.9 Microwave effect on potassium promoted Fe/SiO ₂ catalysts	132
6.9.1 Catalytic activity	132
6.9.2 Carbon dioxide selectivity	133
6.9.3 Methane selectivity	134
6.9.4 Olefin selectivity	135
6.10 Effect of duration on Fe/SiO ₂ catalysts	136
6.10.1 Catalytic activity	137
6.10.2 Carbon dioxide selectivity	139
6.10.3 Methane selectivity	140
6.10.4 Olefin selectivity	141
6.11 Effect of the power level on Fe/K/SiO ₂ catalysts	142
6.11.1 Catalytic activity	142
6.11.2 Carbon dioxide selectivity	143
6.11.3 Methane selectivity	144
6.11.4 Olefin selectivity	145

6.12 E	Effect of bed size and shape on Fe/K/SiO ₂ catalysts	146
	6.12.1 Catalytic activity	146
	6.12.2 Carbon dioxide selectivity	147
	6.12.3 Methane selectivity	148
	6.12.4 Olefin selectivity	149
6.13	Microwave effect on catalytic activity and selectivity of a partially	
	reduced Fe/SiO ₂ catalyst	150
	6.13.1 Activity measurements	151
	6.13.2 Carbon dioxide selectivity	152
	6.13.3 Methane selectivity	153
	6.13.4 Olefin formation	154
6.14 Effect of calcination temperature on catalytic activity and selectivity		
1	for the Fe/SiO ₂ catalyst in FTS	155
	6.14.1 Activity measurements	155
	6.14.2 Carbon dioxide selectivity	157
	6.14.3 Methane selectivity	158
	6.14.4 Olefin selectivity	159
6.15 N	Aicrowave effect on Fe/SiO ₂ catalysts calcined at 700 °C	160
	6.15.1 Catalytic activity	160
	6.15.2 Carbon dioxide selectivity	161
	6.15.3 Methane selectivity	162
6.16 E	Effect of microwave on unsupported iron catalysts (Fe/K)	164
	6.16.1 Fischer-Tropsch synthesis	164

6.16.1.1 Activity measurements	164
6.16.1.2 Carbon dioxide selectivity	165
6.16.1.3 Methane selectivity	166
6.16.1.4 Olefin selectivity	167
6.17 Fischer-Tropsch synthesis: Co/SiO ₂ catalysts	168
6.17.1 Activity measurements	168
6.17.2 Product distribution and selectivity	168
6.18 Summary of catalytic activity, product distribution and selectivity	
6.18.1 Carbon monoxide conversion	170
6.18.2 Carbon dioxide selectivity	171
6.18.3 Methane selectivity	171
6.18.4 Olefin selectivity	171
6.18.5 Chain growth	172
6.18.6 Suggested future work	172
Chapter 7 Conclusion	173
7.1 Catalyst characterization	173
7.2 Fischer-Tropsch reactions	174
7.3 Future work	174
Chapter 8 References	176
LIST OF FIGURES	

2.1 Process overview for transport fuel and chemicals production via

	Fischer-Tropsch synthesis	7
	(FTS)	7
2.2	Alkyl mechanism for initiation and propagation of hydrocarbon chain: (a) methylene formation, (b) initiation of chains, (c) initiated chain growth, (d) propagation (Fernandes, 2005)	12
2.3	Alkyl mechanism for termination of hydrocarbon chains: (a) surface	
2.0	hydride termination giving alkanes, (b) β -elimination mechanism forming α -olefins (Fernandes, 2005)	12
2.4	Alkenyl mechanism: (a) initiation of chain, (b) Chain growth including insertion of methylene and isomerization, (c) propagation of hydrocarbon chains (Fernandes, 2005)	14
2.5	Enol mechanism (Scorch <i>et al.</i> , 1951)	15
2.6	CO insertion mechanism (Hindermann et al., 1993)	16
2.7	Formation of branched hydrocarbons (Schulz et al., 1970)	16
2.8	Synthesis gas conversion as a function of reciprocal flow rate. ○, 0.36 K; □, 1.4 K; ◊, 2.2 K, (Davis et al., 1998)	28
2.9	Deactivation mechanisms A) Coke formation, B) Poisoning, C) Sintering of the active metal particles and D) Sintering and solid-solid phase transitions of the washcoat and encapsulation of active metal particles (Suhonen, 2002)	37
2.10	TPR spectra of the unpromoted and promoted Co/Al ₂ O ₃ catalysts with different loading of rhenium with (light) and without interval calcination (dark)	40
		.0

3.1	SEM images of CO/SiO ₂ catalysts (20kV, x4, 500): (a) silica support, (b) conventional heating catalyst and (c) microwave irradiation catalyst (Reubroycharoen <i>et al.</i> , 2007)	50
5.1	Schematic representation of the rig used for the Fischer-Tropsch Synthesis (FTS), PCI: pressure indicator control, TIC: temperature indicator control, PI: pressure indictor, FID: flame ionization	
	detector, TCD: thermal conductivity detector, to vent (ventilation)	65
5.2	Schematic representation of the reactor used in the FTS	67
5.3	A typical chromatogram obtained from a TCD analysis. H_2 , CO, CH_4 and CO_2 investigated respectively	70
6.1	TEM images of the unsupported catalysts before and after microwave pre-treatment. Iron catalyst was microwave pre-treated at 540 W for 8 s	73
6.2	Crystallite size distribution (nm) of unsupported iron oxide samples before and after microwave pre-treatment. \underline{a} = before microwave pre-treatment, \underline{b} = after microwave pre-treatment	74
6.3	Powder X-Ray diffraction patterns of the unsupported catalysts before and after microwave pre-treatment. Fe ₂ O ₃ containing catalyst was microwave pre-treated at 540 W for 8 s	75

XRD profiles of CoZrO₂ catalysts (Zhao et al., 2003).....

42

2.11

6.4 Surface area and pore volume obtained from unsupported

	catalysts before and after microwave pre-treatment.	
	Microwave pre-treatment was done at different	
	times: 8, 15, 30 and 60 s respectively	76
6.5	Crystallite size (nm) obtained from TEM, PXRD and BET showing	
	the increase in particle size with the microwave heating	
	(540 W for 8 s)	78
6.6	TPR profiles of the unsupported catalysts before and after microwave	
	pre-treatment. Both samples were degassed at 5 °C/ min. in helium	
	for 45 min. and reduced in hydrogen at 10 °C/ min	79
6.7	SEM images of the unsupported catalysts before and after microwave	
	pre-treatment. Microwave pre-treatment was done at 540 W for 8 s	71
6.8	TEM micrographs of partially reduced iron catalysts before and after	
	microwave pre-treatment. The microwave pre-treatment was	
	carried out at 540 W for 8 s	81
6.9	Crystalline size distribution (nm) of unsupported iron oxide	
	samples before and after microwave pre-treatment. $\underline{a} =$ before microwave	
	pre-treatment, \underline{b} = after microwave pre-treatment	82
6.10	PXRD patterns of magnetite containing iron catalysts showing	
	the microwave effect	83
6.11	Crystallite size (nm) obtained from TEM and PXRD for a partially	
	reduced iron catalyst showing the increase in particle size with	
	the microwave heating (540 W for 8 s)	84

6.12	TPR profiles of the partially reduced iron catalysts before and after	
	microwave pre-treatment	85
6.13	TEM images of the Fe/K catalysts before and after microwave pre-	
	treatment. Microwave pre-treatment was carried out at 540 W for 8 s	86
6.14	Crystallite size distribution (nm) of Fe/K samples before and	
	after microwave pre-treatment. \underline{a} = before microwave pre-treatment,	
	$\underline{\mathbf{b}}$ = after microwave pre-treatment	87
6.15	PXRD patterns of the Fe/K catalysts before and after microwave pre-	
	treatment showing the effect of microwave pre-treatment on	
	iron catalysts	89
6.16	Crystallite size (nm) for Fe/K catalysts obtained from TEM and	
	PXRD showing the increase in particle size with the microwave	
	heating (540 W for 8 s)	89
6.17	TEM micrographs of the microwave pre-treated unsupported iron	
	catalysts investigating the effect of the power level.	
	Microwave pre-treatment was carried out for 8 s	90
6.18	Crystallite size distribution (nm) of iron oxide samples microwave	
	pre-treated at different power levels (270, 540 and 900 W) for 8 s	91
6.19	PXRD patterns of the iron catalysts microwave pre-treated at	
	different power levels for 8 s	92
6.20	Crystallite size (nm) obtained from TEM and PXRD showing	

	the increase in particle size with the microwave heating at different power level (270, 540 and 900W)	94
6.21	PXRD patterns for Fe/K catalysts microwave pre-treated at different times. Microwave pre-treated was carried out at 540 W	95
6.22	Crystallite size (nm) obtained from PXRD and BET for Fe/K catalysts showing the increase in particle size with the microwave heating at different times (0, 8,15, and 60 s)	97
6.23	PXRD patterns of the Fe/K catalysts both microwave pre-treated at 540 W for 8 s. Bed size and shape was varied to understand the microwave effect	98
6.24	A TGA profile of the uncalcined Fe/SiO ₂ catalyst	101
6.25	A TPR profile of Fe/SiO ₂ catalyst calcined at 350 $^{\circ}$ C for 6, 5 h in air	102
6.26	PXRD profiles of Fe/SiO ₂ catalyst calcined at different temperatures for 6.5 h in air at 5 °C/min	103
6.27	Transmission Mössbauer spectroscopy (TMS) spectra of Fe/SiO_2 samples before and after potassium promotion taken at room temperature. Enlarged image of the same profiles is displayed in <u>b</u>	105
6.28	Hydrogen temperature-programmed reduction (H ₂ -TPR) profiles of Fe/SiO ₂ catalysts before and after microwave pre-treatment. Microwave pre-treatment was done at 540 W	106
6.29	BET surface area for SiO ₂ support microwave pre-treated at different power levels	108

6.30	PXRD profiles for Fe/K/SiO ₂ before and after microwave	
	pre-treatment	109
6.31	TPSR profiles investigating the microwave effect on Fe/K/SiO ₂ catalysts	110
6.32	TPSR profiles investigating the effect of the power level on	
	Fe/K/SiO ₂ catalyst	111
6.33	SIMS secondary ion intensities against ions present in	
	Fe/K/SiO ₂ catalysts obtained before and after microwave	
	pre-treatment. For the microwave pre-treatment, $Fe/K/SiO_2$	
	catalyst was heated for 8 s at 540 W	112
6.34	CO conversion (%) with time on stream (min.) for the Fe/K/SiO ₂	
	catalysts before and after microwave pre-treatment. Microwave	
	pre-treatment was carried out at 540 W for 8 s	115
6.35	Carbon dioxide selectivity as a function of time on stream for	
	Fe/SiO_2 and $Fe/K/SiO_2$ catalysts. The microwave pre-treatment	
	was carried out at 540 W for 8 s	117
6.36	Methane selectivity in FTS for Fe/SiO ₂ and Fe/K/SiO ₂ catalysts	118
6.37	Molar content of olefins in corresponding fraction of linear	
	hydrocarbons as a function of carbon number in Fischer-Tropsch	
	after 5h time on stream for Fe/SiO ₂ and Fe/K/SiO ₂	122
6.38	CO conversion with time on stream (min.) in the Fischer-Tropsch	
	synthesis for Fe/SiO ₂ catalysts before and after microwave pre-treatment.	
	The microwave pre-treatment was carried out at 540 W for 8 s	123

6.39	Carbon dioxide selectivity as a function of time on stream (min.) for	
	the Fe/SiO ₂ catalysts before and after microwave pre-treatment	124
6.40	Methane selectivity as a function of reaction time on stream (min.)	
	for Fe/SiO_2 catalysts before and after microwave pre-treatment. The	
	microwave pre-treatment was carried out at 540 W for 8 s	125
6.41	Molar content of olefins in corresponding fraction of linear hydrocarbons	
	as a function of carbon number in Fischer-Tropsch synthesis after	
	5h time on stream for Fe/SiO ₂ catalyst before and after microwave	
	pre-treatment. The microwave pre-treatment was carried out	
	at 540 W for 8 s	126
6.42	Changes in carbon monoxide conversion as a function of time on	
	stream (min.) for the Fe/SiO ₂ catalyst precursors before and after	
	microwave pre-treatment. Fe/SiO ₂ catalyst was	
	dried at 110 °C overnight	127
6.43	Carbon dioxide selectivity (%) as a function of time on stream	
	(min.) for the Fe SiO_2 catalysts precursors before and after	
	microwave pre-treatment	128
6.44	Methane selectivity as a function of reaction time on stream (min.)	
	for Fe\SiO ₂ catalyst precursors before and after microwave	
	pre-treatment	129
6.45	Molar content of olefins in corresponding fraction of linear	
	hydrocarbons as a function of carbon number in Fischer-Tropsch	
	after 5h time on stream for Fe/SiO ₂ catalyst precursors before	
	and after microwave pre-treatment	130

6.46	Ethylene conversion (%) as a function of reaction time on stream (h) $(% A = A + A + A + A + A + A + A + A + A +$	
	for the Fe/SiO ₂ catalyst precursors before and after microwave	
	pre-treatment	131
6.47	Changes in CO conversion in the Fischer-Tropsch synthesis as a function	
	of time on stream for Fe/K/SiO ₂ catalysts before and	
	after microwave pre-treatment	132
6.48	CO ₂ selectivity as a function of time on stream in the	
	Fischer-Tropsch synthesis for Fe/K/SiO ₂ catalysts before	
	and after microwave pre-treatment	133
6.49	Methane selectivity in Fischer-Tropsch synthesis for Fe/K/SiO ₂	
	catalysts before and after microwave pre-treatment	134
6.50	Molar content of olefins in corresponding fraction of linear hydrocarbons	
	as a function of carbon number for Fe/K/SiO ₂ catalysts before	
	and after microwave pre-treatment	135
6.51	Changes in CO conversion (%) in the Fischer-Tropsch synthesis as	
	a function of time on stream (min.) for Fe/K/SiO ₂ catalysts microwave pr	e-
	treated at different times (s)	137
6.52	Catalytic activity for Fe/K/SiO ₂ as a function of the time of	
	microwave pre-treatment (s)	138
6.53	Carbon dioxide selectivity as a function of time on stream in the	
	Fischer-Tropsch synthesis for the Fe/K/SiO ₂ catalysts microwave	
	pre-treated at different times at 540 W	139
6.54	Methane selectivity in the Fischer-Tropsch synthesis as a function	

	of time on stream for Fe/K/SiO2 catalysts microwave pre-treatment	
	for 540 W at different times	140
6.55	Molar content of olefins in corresponding fraction of linear	
	hydrocarbons as a function of carbon number in Fischer-Tropsch	
	synthesis for Fe/K/SiO ₂ catalysts microwave pre-treatment	
	at 540 W for different times	141
6.56	Carbon monoxide conversion with time on stream in Fischer-Tropsch	
	synthesis for Fe/K/SiO ₂ catalysts microwave pre-treatment at	
	different power levels for 8 s	142
6.57	Carbon dioxide selectivity as a function of time on stream in the	
	Fischer-Tropsch synthesis for Fe/K/SiO ₂ catalysts	
	microwave pre-treated at different power levels for 8 s	143
6.58	Methane selectivity in the Fischer-Tropsch synthesis as a function of	
	time on stream for Fe/K/SiO2 catalysts microwave pre-treatment at differ	ent
	power level for 8 s	144
6.59	Olefins in linear hydrocarbons as a function of carbon number in	
	Fischer-Tropsch synthesis for Fe/K/SiO2 catalysts microwave	
	pre-treated for 8 s at different power levels	145
6.60	CO conversion against time on stream for Fe/K/SiO ₂ catalysts in the	
	Fischer-Tropsch synthesis. To investigate the microwave effect: in	
	one case the catalyst was placed uniformly in a Petri dish, on	
	the other hand, the catalyst was not being spread	146
6.61	Carbon dioxide selectivity as a function of time on stream in the	
	Fischer-Tropsch synthesis for Fe/K/SiO ₂ catalysts microwave	

	pre-treated	147
6.62	Methane selectivity in the Fischer-Tropsch synthesis against	
	time on stream after both samples were microwave pre-treated	
	with varying bed size and shape	148
6.63	Olefins in linear hydrocarbons as a function of carbon number in	
	the Fischer-Tropsch synthesis for the Fe/K/SiO ₂ catalysts	
	microwave pre-treated with varying bed size and shape	149
6.64	Changes in carbon monoxide conversion in the Fischer-Tropsch	
	synthesis as a function of time on stream for Fe/SiO_2 catalysts partially	
	reduced at 300 °C. FTS experiments were done before and after	
	microwave pre-treatment	151
6.65	Carbon dioxide selectivity as a function of time on stream for	
	the Fe/SiO ₂ catalysts partially reduced at 300 $^{\circ}$ C for 16 h in flowing	
	hydrogen. FTS experiments were done before and after microwave	
	pre-treatment	152
6.66	Methane selectivity in the FTS as a function of reaction time on stream	
	for the Fe/SiO_2 catalysts before and after microwave pre-treatment.	
	Fe/SiO ₂ catalyst was first partially reduced in hydrogen at 300 $^{\circ}$ C for 16 h	•
	This was followed by the microwave pre-treatment	153
6.67	Olefins in linear hydrocarbons obtained from Fe/SiO ₂ catalysts before	
	and after microwave pre-treatment	154
6.68	CO conversion as a function of time on stream for the Fe/SiO ₂ catalysts	
	calcined at different temperatures	155

6.69	Carbon dioxide selectivity as a function of time on stream (min.) for the Fe/SiO_2 catalysts showing the effect of calcination temperature	157
6.70	Methane selectivity (C-%) with time on stream (min.) for Fe/SiO_2 catalysts calcined at different temperatures	158
6.71	Olefins in linear hydrocarbons $(C_2 - C_8)$ obtained from Fe/SiO ₂ catalysts calcined at different temperatures	159
6.72	CO conversion as a function of time on stream for Fe/SiO_2 catalyst calcined at 700 °C. FTS experiments were done before and after microwave pre-treatment.	160
6.73	Carbon dioxide selectivity as a function of time on stream (min.) for the Fe/SiO ₂ catalysts calcined at 700 °C. FTS experiments were carried or before and after microwave pre-treatment	ut 161
6.74	Methane selectivity (C-%) with time on stream (min.) for Fe/SiO_2 catalysts calcined at 700 °C. FTS experiments were carried out before and after microwave pre-treatment	162
6.75	PXRD patterns of the Fe/SiO ₂ catalysts calcined at 700 °C for 6.5 h in air. PXRD experiments were taken before and after microwave pre-treatment.	163
6.76	CO conversion as a function of time on stream in the FTS for Fe/K catalysts before and after microwave pre-treatment. Microwave pre-treatment was carried out at 540 W for 8 s	164
6.77	CO ₂ selectivity as a function of time on stream in the FTS for Fe/K catalysts before and after microwave pre-treatment	165

6.78	Methane selectivity against reaction time on stream for Fe/K	
	before and after microwave pre-treated	166
6.79	Olefins in linear hydrocarbons as a function of time on stream for	
	Fe/K catalysts before and after microwave pre-treatment. Microwave	
	pre-treatment was carried out at 540 W for 8 s for the microwave	
	pre-treated catalyst	167

LIST OF TABLES

2.1	Approximate relative price of metals for FTS in 2004 (Dry, 2004)	24
3.1	Catalytic activity of conventional and microwave cobalt catalysts on Fischer-Tropsch synthesis (FTS)	51
5.1	A list of columns used in FTS and analysis conditions	71
6.1	Surface area determination investigating the effect microwave pre-treatment on Fe/K catalysts	88
6.2	Surface area determination investigating the effect of the power level on Fe/K catalysts. Duration for the microwave pre-treatment was kept constant, 8 s for all the experiments	93
6.3	Surface area determination investigating the effect of duration on Fe/K catalysts	96
6.4	Surface area determination investigating the effect of the bed size and shape on promoted iron oxide catalysts	99

6.5	Elemental composition of the calcined, supported Fischer-Tropsch	
	catalysts	100
6.6	BET surface areas of the Fe/SiO ₂ catalyst with and without potassium promotion at different potassium loading	104
6.7	BET surface areas for the Fe\SiO ₂ catalyst before and after microwave pre-treatment	107
6.8	Chain growth probabilities obtained from Fe/SiO ₂ and Fe/K/SiO ₂ catalysts	121
6.9	Chain growth probabilities obtained from Fe/K/SiO ₂ catalysts before and after microwave pre-treatment	136
6.10	Surface area determination for Fe/SiO ₂ catalysts calcined at different temperatures	156
6.11	Chain growth probability, α (%) for Co/SiO ₂ catalysts before and after microwave pre-treated at 900 W for 15	168
6.12	Information taken from C_5 for the Co/SiO ₂ catalysts before and after microwave pre-treatment at 900 W for 15 s	169

ABSTRACT

The main aim of this work was to investigate the microwave effect on catalytic activity and selectivity in Fischer-Tropsch synthesis. Characterization techniques for bulk analysis such as TEM, PXRD and BET revealed that there is a significant increase in the particle size of iron catalysts due to the microwave pre-treatment. TPR, SEM showed no significant change in the reducibility and morphology after microwave pre-treatment of the iron catalysts. However, high surface sensitive techniques such as: temperature programmed surface reactions (TPSR) and Secondary ion mass spectroscopy (SIMS) experiments are more revealing the changes which take place on the catalyst surface. SIMS measurements showed that the ratio of Fe:K increases from 0.06 to 0.1 after the microwave pre-treatment. This shows that the microwave pre-treatment alters the surface of the iron FT catalysts. Temperature-programmed surface reactions investigated that the microwave pre-treatment increases the number and type of active sites present on the catalyst surface. The amount of the desorbing components from the catalyst surface was found to increase with the microwave pre-treatment also.

Effect of the power level was studied, TPSR investigated that 270 W is the optimum power to be used in the microwave pre-treatment of the Fe/SiO_2 catalysts in order to obtain significant microwave effect.

Positive effects on product selectivity such as: decrease in methane selectivity, enhanced carbon dioxide selectivity and improvement in the formation of olefins were observed after microwave pre-treatment. The formation of methane dropped due to the crystal growth which takes place after microwave heating. An increase in carbon dioxide selectivity was claimed to be due to high conversion level obtained after microwave pre-treatment of a potassium promoted iron catalysts. Enhancement in the formation of olefins was found to be due to promotion effect. The microwave pre-treatment affects the way in which iron and potassium interact.