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

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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

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Presentations

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- CATSA 2008: Poster presentation: “Effect of the power level on catalytic activity and selectivity on Fischer-Tropsch synthesis”.

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- 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…….. 18

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……. 22

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

Chapter 3 Microwave chemistry 46

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…… 71

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

6.6 Summary of the characterization results of iron catalyst and conclusion… 113

6.7 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

6.8 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^oC)……. 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 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 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 Microwave effect on Fe/SiO_2 catalysts calcined at 700 ^{o}C……... 160

6.15.1 Catalytic activity……. 160

6.15.2 Carbon dioxide selectivity…….. 161

6.15.3 Methane selectivity……. 162

6.16 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……. 170

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
(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 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 *et al*., 1951)……. 15

2.6 CO insertion mechanism (Hindermann *et al*., 1993)…… 16

2.7 Formation of branched hydrocarbons (Schul*z 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_2O_3 catalysts with different loading of rhenium with (light) and without interval calcination (dark)……. 40

2.11 XRD profiles of $CoZrO_2$ catalysts (Zhao et al., 2003)…….. 42

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 *et al*., 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. a = before microwave pre-treatment, b = after microwave pre-treatment……... 74

6.3 Powder X-Ray diffraction patterns of the unsupported catalysts before and after microwave pre-treatment. Fe_2O_3 containing catalyst was microwave pre-treated at 540 W for 8 s…… 75

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 ^{o}C/ min. in helium for 45 min. and reduced in hydrogen at 10 ^{o}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. a = before microwave pre-treatment, 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. a = before microwave pre-treatment, 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 ^oC 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 ^oC/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 b…. 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 ^{o}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) 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 pre-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/SiO_2 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/SiO_2 catalysts microwave pre-treatment at different 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/SiO_2 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 ^{o}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 ^{o}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 ^{o}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 ^oC. 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 ^oC. FTS experiments were carried out before and after microwave pre-treatment……... 161

6.74 Methane selectivity (C-%) with time on stream (min.) for Fe/SiO_2 catalysts calcined at 700 ^oC. 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 ^oC 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.