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.

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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

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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.