Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

…….

Signature of candidate

……. day of …… 2012

Abstract

Microwave-assisted pre-treatment is a fast, selective and volumetric method used to activate catalysts. The advantages of using microwave radiation emanate from its ability to transfer energy directly to the reactive species (called molecular heating), thereby promoting transformations that are not possible using conventional heating. In this work the unique microwave heating properties have been used for the modification of iron-based Fischer-Tropsch catalysts in the solid state. The effect of the potassium loading on the microwave effect is presented.

A series of unsupported and silica supported iron FT catalysts were prepared using the continuous precipitation and the incipient wetness impregnation techniques. The amount of the potassium promoter was varied from 0.2 to 1.5 wt. % in the catalysts. Microwave pre-treatment (10 seconds, 450 W) was then done prior to catalyst characterization and evaluation. The bulk properties of the catalysts were characterized using XRF, BET, TPR, XRD, TEM and EDS techniques and the surface properties were determined by temperature programmed surface reaction-mass spectrometry (TPSR-MS). The results showed that microwave pre-treatment modified the surface but not the bulk properties of the K/Fe and the K/Fe/SiO_2 catalysts. Catalytic properties of the catalysts were evaluated using FTS and increases in the olefin selectivity and the α value were found with the microwaved catalysts. Differences in the data recorded for the microwaved and the non-microwaved samples were taken to be induced by microwave pre-treatment since all other parameters were kept constant in all reactions.

TPSR profiles (methane profiles) were used to study the carbon chemisorption behaviour of the catalyst surface. Peak areas were used to determine the type and amount of carbon species deposited on the catalyst. Microwave pre-treatment was seen to increase the amount of methane produced in the TPSR experiments, indicative of an increase in the number of active sites. The increase was observed to be dependant on the potassium loading in the catalyst. It is suggested that microwave modification promotes the migration of potassium ions to the surface of the catalyst. The effects of the microwave irradiation time and the catalyst preparation method were also investigated.

To my parents Eve Dzeliwe Dlamini

And

the late Morris Mehlwengane Dlamini

And the rest of my family members

I love you all

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University of Swaziland

The Almighty God, with whom all things become possible

Presentation at seminars and conferences

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- November 2010: Awarded **best (1st place) MSc oral presentation** at the South African Chemical Institute (SACI) Young Chemist Symposium hosted by SACI and the Royal Society of Chemistry at the University of Johannesburg
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Publications arising from this work

1. M. W. Dlamini, M. S. Scurrell, N. J. Coville, *"Temperature programmed surface reaction as a means of investigating the microwave effect in precipitated Fischer-Tropsch synthesis catalysts"* To be submitted

2. M. W. Dlamini, M. S. Scurrell, N. J. Coville, *"The effect of potassium on microwave modified silica-supported Fischer-Tropsch synthesis catalysts"* To be submitted

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Abbreviations and acronyms

Anderson, Schultz, Flory	ASF
Badische Anilin-und Soda Fabrik	BASF
Barrett-Joyner-Halenda	BJH
Brunuaer, Emmet, Teller	BET
Carbon dioxide	CO_2
Carbon monoxide	CO
Carbon nanotube	CNT
Chain growth probability	α
Circulating fluidized bed	CFB
Conventional heating	CH
Degrees Celsius	^oC
Deposition precipitation	DP
Energy dispersive X-ray spectroscopy	EDS
Fischer-Tropsch	FT
Fischer-Tropsch Synthesis	FTS
Flame ionization detector	FID
Fluidized fixed bed	FFB
Gas chromatograph	GC
Gas to liquids	GTL
Hydrogen	H_2
International union of pure and applied chemistry	IUPAC
Iron	Fe
Iron (III) nitrate nonahydrate	$Fe(NO_3)_3.9H_2O$
Mass spectrometry	MS
Methane	CH_4

Microwave	MW
Microwave-assisted organic synthesis	MAOS
Mossbauer emission spectroscopy	MES
Nitrogen	N_2
Oxidative coupling of methane	OCM
Percentage	%
Potassium	K
Powder X-ray diffraction	PXRD
Quadrupole mass spectrometer	QMS
Sasol Advanced Synthol	SAS
Secondary ion mass spectrometry	SIMS
Shell middle distillate synthesis	SMDS
Temperature programmed reduction	TPR
Temperature programmed surface reaction- mass spectrometry	TPSR-MS
Thermal conductivity detector	TCD
Transmission electron microscopy	TEM
Ultra-high purity	UHP
Water gas shift	WGS
Watts	W
Weight percentage	wt. %
X-Ray fluorescence	XRF