

**CATALYTIC CONVERSION OF SYNTHESIS GAS TO
FUEL OVER Cu-K PROMOTED AND $\text{SiO}_2/\text{Al}_2\text{O}_3$
SUPPORTED Fe CATALYSTS**

SATYEN KUMAR DAS



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

September, 2013

**CATALYTIC CONVERSION OF SYNTHESIS GAS TO
FUEL OVER Cu-K PROMOTED AND $\text{SiO}_2/\text{Al}_2\text{O}_3$
SUPPORTED Fe CATALYSTS**

by

SATYEN KUMAR DAS

Department of Chemical Engineering

*Submitted in fulfillment of
the requirements of the degree of*

DOCTOR OF PHILOSOPHY

to the



Indian Institute of Technology Delhi

September, 2013

DEDICATED

TO

MY BELOVED FAMILY

CERTIFICATE

This is to certify that the thesis entitled, “**CATALYTIC CONVERSION OF SYNTHESIS GAS TO FUEL OVER Cu-K PROMOTED AND $\text{SiO}_2/\text{Al}_2\text{O}_3$ SUPPORTED Fe CATALYSTS**” being submitted by **Mr. Satyen Kumar Das** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy is a record of bonafide research work carried out by him under my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology, Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

(Dr. K. K. Pant)
Professor
Department of Chemical Engineering
Indian Institute of Technology, Delhi
New Delhi-110016

ACKNOWLEDGMENTS

At this moment, these are the thoughts that come to my mind to express my deep sense of gratitude to Prof. Kamal Kishore Pant, Department of Chemical Engineering, Indian Institute of Technology, Delhi by whose inspiration, keen interest and kind support, I had the opportunity to conduct this study. I shall be indebted to him forever for inculcating within me the qualities of perseverance, confidence and a sense of commitment towards one's work. Without his unconditional support, this task couldn't have been so easy for me. I specially thank him for being kind and considerate towards me throughout the course of this work. It was a fortunate and unforgettable experience to work under his reflective and revered guidance. His endless kindness and incomparable support cannot be thanked adequately here.

The encouragement, constant support, critical reviews and important suggestions given by Prof. James Gomes, Prof. A. N. Bhaskarwar, Dr. Sreedevi, Prof. S. Roy, Prof. A. K. Gupta, Prof. S. Basu (current Head of the Department), Prof. R. Khanna, Prof. A. K. Saroha and Dr. V. V. Buwa throughout my research work are greatly acknowledged.

I was fortunate to have an excellent work environment in the laboratory, which facilitated my work to a great deal. For this, I must thank Mr. N. K. Gupta, lab superintendent, Mr. Sachchit Kumar Majhi and Mr. Pravakar Mohanty for their constant help in every possible way to carry forward my research work. I am extremely thankful to Mr. Sushil Saraswat, Mr. Dinesh Kumar, Mr. Snehal Parmar, Ms. Sonal, Mr. Rohit, Mr. Vishesh Kumar and Mr. Krishan Kumar for their help and assistance rendered with the laboratory facilities during the different stages of the experimental work. I also wish to thank the other faculty members and office staff of the Department.

I am thankful to Mr. Murali, Mr. Mrunal and Mr. Salim for their unstinted support, love and concern right from our course work days. Life at IIT, Delhi would have been boring without Sachchit and Pravakar, true friends in the real sense of the word. Their lively companionship made my research work a really enjoyable experience. Their cooperation, concern and encouragement in their own little ways actually pulled me through the tougher and trying times. I must thank my friends and colleagues Sanjay, Vikrant Sarin and Nandini for keeping a cordial environment in the lab and providing fruitful suggestions. I would like to thank Sachchit and Pravakar additionally for helping me with the final editing of this thesis. I am also thankful to Tarak Mondal, Vaibhav, Anshul, Mohit Khatri, Omkarram, Deepak Pal, Suchit Kumar Pal and other students for their kind concern and support.

I would like to thank Dr. R. K. Malhotra (Director, IOCL R&D) to permit for my Ph.D. studies and perform my part of experimental work at R&D Center. He also encouraged me a lot during the period of my Ph.D. studies and helped whenever needed. I am especially thankful to Dr. S. Ghosh (Ex-Executive Director, IOCL R&D) and Dr. R. P. Verma (Ex- Executive Director, IOCL R&D), Dr. A. K. Das (Vice President, Reliance R&D), Mr. S. Mandal (Asst. Vice President, Reliance R&D), Mr. B. S. Rawat (Ex-General Manager, IOCL R&D), and Dr. M. Santra (Ex- Chief Research Manager, IOCL R&D) for their constant help and support.

I would like to make a special mention to Dr. M. B. Patel, Dr. Christopher, Dr. Anju Chopra, Dr. Sova Bhattacharyya, Mrs. Vatsala, Mr. Eswar P. Dalai, Mr. J. K. Dixit, Mrs. M. M. Moulik, Mr. G. Saidulu, Mr. R. M. Thakur, Dr. M. Sau, Mr. D. Bhattacharya, Mr. S. Singh and Mr. Brijesh Kumar (IOCL R&D) who was always there to help me when needed. When one owes so many, it is almost impossible and invidious

to single out names. However, I acknowledge my well-wishers and friends Dr. S. Santra, Mrs. J. Kar, Mr. Biswanath, Mr. K. Ramesh, Mr. G.S. Mishra, Mr. Hillol, Dr. I. R. Chaudhary, Dr. Tapan Bera, Mr. D. P. Dalai, Mr. Mainak Sarkar, Mr. L. L. Saroya, Mr. THVD Prasad, Mr. Pradeep P.R. and H. Belwal for inspiring me throughout my Ph. D. work. The frequent lab get-togethers with all my friends and colleagues brightened up things.

I cannot, but feel indebted towards my wife Maya and son Sayan. Her unconditional and kind support in looking after my son right from his birth to date actually helped me to work consistently and concentrate on my work. My son's innocent smile and baby talk was a constant source of encouragement. I am also thankful to parents, brother, sisters and my relatives, for their constant encouragement and support during my studies.

I will always be indebted to my wife, Maya for realizing my goals. Her continuous optimism, patience and faith from the commencement till the completion of this work are invaluable. I cannot forget her immense support in all odd and even situations. She lightened my burden by sharing my domestic responsibilities. She has been the principal motivating force in this endeavor for which no words of thanks would be sufficient.

I would also like to thank my critics who have unknowingly helped me to come out as a better professional and individual.

Herewith I would like to thank all of those, who have directly or indirectly contributed to the realization of this thesis.

Last but not the least, a note of heartfelt devotion to GOD, who has made me capable of accomplishing this uphill task.

(Satyen Kumar Das)

ABSTRACT

Fischer–Tropsch synthesis (FTS) for converting syngas to hydrocarbons is receiving renewed attention, driven by the global need to convert non-petroleum based energy resources into gaseous & liquid fuels, waxes and chemicals. It is well recognized that the research and the development of catalysts play a vital role in all process of catalysis reaction. In the present investigation, different K and Cu promoted Fe/SiO₂ and Fe/Al₂O₃ catalyst formulations were prepared by varying Fe/Cu/K loading using a combination of co-precipitation and impregnation techniques. The characterization of fresh, reduced and spent catalysts was performed to identify their textural properties, surface morphologies and chemisorptions properties. The characterization was done by inductively coupled plasma analyzer, N₂ adsorption/desorption isotherm, BET surface area, pore volume, BJH pore size distribution measurements, temperature programmed reduction, H₂-chemisorptions, NH₃-temperature programmed desorption, X-ray diffraction; fourier transform infrared spectroscopy, thermogravimetric analysis, carbon hydrogen nitrogen sulphur analyzer, scanning electron microscope, energy dispersive X-ray (quantity & X-ray mapping), transmission electron microscopy techniques. The initial FT synthesis experiments were designed to evaluate each catalyst under fixed and representative conditions from which the most promising catalyst was selected for further study. Their catalytic performance of each catalyst was compared. The screening tests were carried out in a fixed bed reactor. Before screening test, each catalyst was reduced in situ with a flow of high purity hydrogen at 220°C for 6 h under atmospheric pressure. The flow rate of H₂ was maintained at 200 ml/g Fe /min in the fresh catalysts. Screening test of each catalyst was carried out at temperature of 245°C, pressure of 15 bar at space velocity of syngas, 33 ml/g cat/min. and H₂/CO inlet molar ratio = 2:1. Effects of metal loading, support, promoter on carbon monoxide conversion, product selectivity (distribution) were studied. The results of the various characterization techniques were used to relate the observed catalytic performance and stability to the catalyst property. The catalytic activity during FTS for SiO₂ support is higher than Al₂O₃, because of higher degree of reduction. Water gas shift activity of SiO₂ supported catalyst is lower than Al₂O₃ supported catalyst due to decreased Fe/K contact owing to the high catalyst surface area of silica supported catalyst. Branched hydrocarbon, olefin and the aromatic content in liquid products, in the presence of Al₂O₃ is higher due to higher acidity of Al₂O₃ supported catalyst. It has been observed that incorporation of K to Fe/SiO₂ catalyst resulted in enhancement of metallic active sites due to higher dispersion. Incorporation of K and Cu favors the reducibility of the catalyst. Increase in active components (Cu-K) in catalyst had a diminishing effect of surface acidity. Also higher K loading had diminishing effect on textural properties. Increasing silica content, the metal support interaction increased.

During FTS, the CO conversion increased significantly with an increase in potassium loading up to 1 wt.% and passed through the maximum at the potassium loading near to 1 wt.%. Further increasing or decreasing potassium loading, a monotonic decline in catalyst activity is observed. Catalyst with ~1% K loading shows the uppermost CO conversion (56.3 wt%). Water Gas Shift activity increased with increase in K loading in the catalyst. The selectivity of C₅+ hydrocarbons increased and lighter hydrocarbons (methane & C₂-C₄) decreased with increase in K-content as well as decrease in silica content in the catalyst. Also increasing K content in the catalyst, olefin selectivity increased and olefin isomerization activity decreased. Catalyst with higher K content showed higher carbon range products as compared to less K promoted catalysts. Higher K content in the catalyst increases the secondary reaction due to which coke on spent catalyst as well as olefinicity nature of coke increased. Increasing K loading, decrease in acidity of the catalysts, increases immovable coke on the spent catalyst. Based on the above studies, silica supported catalyst with 1% K loading (Catalyst Cat-1K, Fe/Cu/K, wt%: 35.5/3/1) was selected for parameter study.

Parameter studies were conducted in a fixed bed reactor with mixture of H₂ and CO in a temperature range from 215 to 245°C, the pressure range of 5-25 bar, the space velocity range of 1000-4000 cc/g cat/h and a H₂/CO feed ratio of 0.7/1–3/1 (mol/mol) to investigate the influence of the above process parameters on the performance of selected Cu-K promoted silica supported Fe based catalyst in terms of its %CO conversion, product selectivity, rate, liquid hydrocarbon product distribution and composition.

Increasing reaction temperature from 215°C to 245°C, higher yields of once-through hydrocarbon products are produced, whereas the content of CO₂, light hydrocarbon gases and olefins is higher. Increase of reaction temperature, the Anderson Schulz Flory (ASF) chain growth probability decreased. Reactor pressure has a significant effect on CO conversion and liquid hydrocarbon yields in the range investigated. With increase in pressure from 5 to 25 bar, the selectivity to the liquid hydrocarbons (C₅+) increased substantially, while the selectivity to methane, C₂-C₄ gaseous product & CO₂ decreased. Increase of reaction pressure, the chain growth probability increased. Increase in space velocity from 1000 to 4000 cc/g cat/hr, CO conversion decreased, selectivity of CH₄, C₂-C₄ and CO₂ is enhanced. CO conversion passed through maxima with the increase of the H₂/CO molar feed ratios from 0.7/1 to 3/1. Increasing H₂/CO ratios in the reactor result in higher amount of lighter hydrocarbons, lower selectivity of C₅+ and olefins. Chain growth probability decreased with increasing H₂/CO ratio. With increase of temperature and space velocity, selectivity of olefins to paraffins increased while

the reversed was observed with increase in pressure and H_2/CO molar ratio. The identification of different key components present in liquid products formed was done by GC-MS Method.

The effects of reaction conditions on the reaction rates are also studied. It was observed that FTS reaction rate (hydrocarbon formation rate) increased with increase in temperature, pressure and GHSV. However, FTS rate passed through optimum with increase in H_2/CO feed ratio from 0.7/1–3/1 (mol/mol). Water Gas Shift activity rate (CO_2 formation rate) increased with increase in temperature and GHSV, while decreased with increase in pressure, H_2/CO molar ratio. From the rate analysis, the optimum operating condition ($T = 225\text{ }^{\circ}C$, $P = 25\text{ bar}$, H_2/CO ratio = ~ 1.2 and GHSV-2000 cc/g cat/h) for FT synthesis of selected silica supported Fe based catalyst (Catalyst Cat-1K: Fe/Cu/K, wt%: 35.5/3/1) was selected. The selected catalyst was tested at the above optimum operating conditions. At optimized operating condition, CO conversion was 45.9 wt.% once through mode operation and C_5+ selectivity for selected catalyst was 77.4 %.

To study the effect of run time on catalyst performance, stability measurement for the selected silica supported Fe based catalyst (Catalyst Cat-1K: Fe/Cu/K, wt%: 35.5/3/1) was investigated at temperature of $245\text{ }^{\circ}C$ with $H_2/CO = 2:1$, GHSV of 2000 cc/g cat/h and a total pressure of 15 bar for 130 h time on stream. No appreciable deactivation was observed for the catalyst at the above operating condition after 130 h run. The spent catalyst was characterized to understand the structural changes that might have occurred during FT synthesis, amount & nature of coke formation. Analysis revealed that mixture of magnetite, iron carbide and iron are the final phases of Fe based FT catalyst. Ultimately, a most promising catalyst is developed along with suitable operating domain for production of fuel from synthesis gas generated from coal, pet coke and biomass.

TABLE OF CONTENTS

	Page No.
Certificate	I
Acknowledgments	II
Abstract	V
List of Figures	XVII
List of Tables	XXI
Nomenclature	XXIII
 CHAPTER 1: INTRODUCTION	
1.1 Background	1
1.2 Fischer Tropsch synthesis	5
1.3 Objectives of the present study	7
1.4 Structure of the Thesis	8
 CHAPTER 2: LITERATURE REVIEW	
2.1 Background of the Fischer Tropsch Synthesis	10
2.1.1 Reactors for Fischer-Tropsch Synthesis	15
2.2 Process route and thermodynamics	18
2.3 Fischer Tropsch Catalysts	22

2.3.1	Water Gas Shift Activity	25
2.3.2	Ruthenium catalysts	25
2.3.3	Nickel catalysts	26
2.3.4	Cobalt catalysts	26
2.3.5	Iron catalysts	27
2.3.6	Catalyst Preparation Method	30
2.3.7	Influence of Support	32
2.3.8	Effect of Promoters and other Additives	34
2.4	Catalyst Pretreatment	38
2.5	FT catalyst deactivation	39
2.5.1	Metal-Support compound formation	40
2.5.2	Attrition/Crushing	41
2.5.3	Conversion of Active Phases to Inert Phases	41
2.5.4	Poisoning	42
2.5.5	Sintering	42
2.5.6	Fouling	43
2.5.7	Carbon Deposition	43
2.6	Product characteristics	44

2.7	Reaction Mechanism	47
2.8	Reaction Kinetics	51
2.9	Influence of process conditions on the product selectivity	53
2.9.1	Temperature	54
2.9.2	Partial pressure of H ₂ and CO	55
2.9.3	Space velocity	56
2.9.4	Time on stream	57
2.9.5	Reduction of the catalyst	57
2.10	Previous studies using Iron based Catalysts	58
2.11	Summary of the Literature Review	60
2.11.1	Gaps from literature search	61
 CHAPTER 3: EXPERIMENTAL DETAILS		
3.1	Catalyst preparation	63
3.1.1.	Synthesis of Fe-Cu-K/SiO ₂ catalysts	64
3.1.2.	Synthesis of Fe-Cu-K/Al ₂ O ₃ catalyst	65
3.1.3.	Preparation of Fe-Cu-K/SiO ₂ catalysts with different K loading	66
3.2.	Catalyst characterization	67
3.2.1.	Determination of elements in catalysts	67

3.2.2.	BET surface area, Porosity and BJH analysis	68
3.2.3.	Temperature programmed and pulse chemisorption studies	68
3.2.4.	Temperature Programmed Desorption (NH ₃ -TPD)	69
3.2.5.	X-ray powder diffraction (XRD)	70
3.2.6.	Fourier transform infrared spectroscopy (FTIR)	70
3.2.7.	SEM-EDAX-X-ray mapping	71
3.2.8.	Transmission Electron Microscopy (TEM)	71
3.2.9.	Thermogravimetric Analysis (TGA)	72
3.2.10.	CHNS Analyzer	72
3.3.	Catalytic activity & selectivity tests, parameter study and stability measurements	72
3.3.1.	Experimental Set-up	73
3.3.2.	Catalyst Selection Procedure	74
3.3.2.1.	FT Synthesis Catalyst Screening Tests	74
3.3.2.2.	FT Synthesis Parameter Study	75
3.3.3.	Stability measurements	76
3.3.4.	Gaseous and Liquid product analysis	77
 CHAPTER 4: RESULTS AND DISCUSSION		
4.0.	Introduction	79

4.1.	Effect of active components using silica supported catalysts	80
4.1.1.	Catalyst characterization	81
4.1.1.1.	Elemental analysis (ICP analysis)	81
4.1.1.2.	BET surface area and pore size distribution	82
4.1.1.3.	Pulse chemisorption analysis	83
4.1.1.4.	Temperature programmed reduction analysis	84
4.1.1.5.	Temperature programmed desorption analysis (TPD-NH ₃)	86
4.1.1.6.	XRD analysis	87
4.1.1.7.	Surface morphology analysis	89
4.1.1.7.1.	SEM analysis	89
4.1.1.7.2.	Particle size analysis	90
4.1.1.7.3.	EDX analysis	91
4.1.1.7.4.	X-ray mapping	92
4.1.1.8.	FT-IR analysis	94
4.1.2.	Catalytic activity and selectivity of Fe/SiO ₂ catalysts	95
4.1.2.1.	Olefins/paraffin selectivity ratio	97
4.1.2.2.	Olefin isomerization activity	98
4.1.3.	Summary of the study	98

4.2.	Effect of supports	99
4.2.1.	Catalyst characterization	99
4.2.1.1.	Elemental analysis (ICP analysis)	99
4.2.1.2.	BET surface area and pore size distribution (BJH isotherm)	100
4.2.3.	Pulse chemisorptions analysis	101
4.2.4.	Temperature programmed reduction analysis (TPR)	102
4.2.5.	Temperature programmed desorption analysis (TPD-NH ₃)	104
4.2.6.	X-ray diffraction	105
4.2.7.	Surface morphology analysis	107
4.2.7.1.	SEM analysis	107
4.2.7.2.	X-ray mapping	108
4.2.8.	Catalytic activity and selectivity	109
4.2.9.	Properties of liquid hydrocarbon	113
4.2.10.	Summary of the study	114
4.3.	Effect of K loading on the most probable catalyst	114
4.3.1.	Catalyst characterization	115
4.3.1.1.	Elemental analysis (ICP-MS analysis)	115
4.3.1.2.	BET surface area and pore size distribution	115

4.3.1.3.	Temperature programmed reduction (TPR)	117
4.3.1.4.	Temperature programmed desorption analysis (NH ₃ -TPD)	119
4.3.1.5.	XRD analysis	120
4.3.2.	Surface morphology study	121
4.3.2.1.	SEM-EDX analysis	121
4.3.2.2.	TEM analysis	122
4.3.3.	Effect of K promoters on activity and selectivity	124
4.3.3.1.	Catalytic activity and selectivity	124
4.3.3.2.	Olefin Selectivity	127
4.3.4.	Summary of this study	128
4.4.	Effect of reaction parameters (Catalyst Cat-1K- Fe/Cu/K, wt%:35.5/3/1)	129
4.4.1.	Effects of temperature on conversion and product selectivity	130
4.4.2.	Effect of pressure	135
4.4.3.	Effect of GHSV	140
4.4.4.	Effect of H ₂ /CO molar ratio	145
4.4.5.	Effect of operating condition on rate	149
4.4.6.	Effect of operating conditions on C ₅ + product properties	154
4.4.7.	Summary of the reaction parameter study	155

4.5.	Liquid product distribution	156
4.5.1.	Effect of temperature	157
4.5.2.	Effect of pressure	159
4.5.3.	Effect of GHSV	161
4.5.4.	Effect of H ₂ /CO ratio	163
4.5.5.	Effect of catalyst support	165
4.5.6.	Carbon number distribution of liquid product	167
4.5.7.	Major Liquid hydrocarbon analysis	168
4.5.8.	Summary of liquid product distribution study	170
4.6.	Catalyst deactivation study	170
4.6.1.	Effect of time on streams on activity	171
4.6.2.	Characterization of spent Cat-1K catalyst	172
4.6.2.1.	Analysis by EDX	172
4.6.2.2.	XRD analysis	172
4.6.2.3.	TG/DTG analysis of spent catalyst	173
4.6.2.4.	CHNS Analysis of spent catalysts	175
4.6.3.	Summary of the deactivation study	175

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions 177

5.2. Recommendations 179

REFERENCES 180

APPENDICES AND PUBLICATIONS 203