

การเปลี่ยนเนื้อหาออลให้เป็นแก๊ลโซลีสันบนทัวเร่่งปฐกิริยาawanada.com



นายธงชัย เมธนาวิน

วิทยานิพนธ์นี้เป็นล้วนหนึ่งของการศึกษาตามหลักสูตรปรัชญา วิគาระมคำลัตธรรมมหาปัลติต

ภาควิชาawiค่าวาระมเมคี

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2527

ISBN 974-563-091-8

009738

I 15816782

THE CONVERSION OF METHANOL TO GASOLINE OVER
VANADOSILICATE CATALYSTS

Mr. Dhongchai Medhanavyn

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Engineering
Department of Chemical Engineering
Graduate School

Chulalongkorn University

1984

The Thesis Title is The Conversion of Methanol to Gasoline over
Vanadosilicate Catalysts

By Mr. Dhongchai Medhanavyn

Department Chemical Engineering

Thesis Advisor Assist. Prof. Piyasan Praserthdam, Dr.Ing.
Prof. Tomoyuki Inui, Dr.Eng.



Accepted by the Graduate School, Chulalongkorn University
in partial fulfilment of the requirements for the Master's degree.

S. Bunnag Dean of Graduate School

(Assoc. Prof. Supadit Bunnag, Ph.D.)

Thesis Committee

..... Woraphat Arthayudh Chairman

(Assist. Prof. Woraphat Arthayukti, Dr. Ing.)

Tonyuki Inui Member

(Prof. Tomoyuki Inui, Dr.Eng.)

... Bigass..... banditd..... Member

(Assist. Prof. Piyasan Praserthdam, Dr.Ing.)

Miwut Santhapanichakoon Member

(Assoc. Prof. Wiwut Tanthapanichakoon, Ph.D.)

U. B. Buel Member

(Dr. Ura Pancharoen)

C. Phischthal Member

(Dr. Charunya Phichitkul)

หัวข้อวิทยานิพนธ์ การเปลี่ยนเมืองอลให้เป็นแก๊สโซลินบันตัวเร่งปฏิกิริยาawanatoซีลเคก
 ชื่อผู้ลิตร นายธงชัย เมธนาวิน
 อาจารย์ที่ปรึกษา ผู้ช่วยศาสตราจารย์ ดร. ปิยะลักษ์ ประเสริฐธรรม
 อาจารย์ที่ปรึกษาร่วม ศาสตราจารย์ ดร. โภโนมย กิ อินูวิ
 ภาควิชา วิศวกรรมเคมี
 ปีการศึกษา 2526



บทคัดย่อ

วิทยานิพนธ์นี้เป็นการศึกษาวิธีการ เตรียมตัวเร่งปฏิกิริยาawanatoซีลเคก เพื่อ ใช้ในการเปลี่ยนเมืองอลให้เป็นแก๊สโซลินที่ความดัน 1 บรรยากาศ ซึ่งในการศึกษาครั้งนี้ ได้เตรียมตัวเร่งปฏิกิริยาawanatoซีลเคกที่อัตราส่วนทางประจุของซิลิคอนต่อวานาเดียมต่างๆ คือ อินดิฟท์, 3,200, 1,600, 400, 90 และ 40 ทั้งนี้ตัวเร่งปฏิกิริยาเหล่านี้ได้ถูกทำการทดลองเพื่อหาลักษณะการทำงานที่เหมาะสม โดยการแปรเปลี่ยนค่าของตัวแปรต่างๆ เช่น ความเร็วเชิงลับช (ระหว่าง 500 ถึง 8,000 ต่อ ชั่วโมง) อุณหภูมิของปฏิกิริยา (ระหว่าง 260 ถึง 420 องศาเซลเซียล) และความเข้มข้นของเมืองอล (ระหว่าง 5 ถึง 100 เปอร์เซนต์) นอกจากนี้ได้ทำการตรวจน้ำความล้มเหลวระหว่างคุณลักษณะทางกายภาพกับ พฤติกรรมทางความเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาสังเคราะห์เหล่านี้ จากผลการทดลองและ การตรวจวัดพบว่า ในอัตราส่วนทางประจุที่เหมาะสมล่มระหว่างซิลิคอนต่อวานาเดียม ตัวเร่งปฏิกิริยาawanatoซีลเคก จะมีคุณภาพในการเปลี่ยนเมืองอลเป็นแก๊สโซลินได้ดีกว่าตัวเร่งปฏิกิริยา ZSM-5

Thesis Title The Conversion of Methanol to Gasoline over
Vanadosilicate Catalysts

Name Mr. Dhongchai Medhanavyn

Thesis Advisor Assistant Professor Piyasan Praserthdam, Dr.Ing.

Thesis Co-advisor Professor Tomoyuki Inui, Dr.Eng.

Department Chemical Engineering

Academic Year 1983



ABSTRACT

The purpose of this study was to determine a preparation method of vanadosilicate catalysts which could be used for a Methanol to Gasoline (MTG) Conversion process at atmospheric pressure. For this purpose, vanadosilicate catalysts which had Si/V charged ratios of ∞ 3200, 1600, 400, 90 and 40 were prepared.

These catalysts were tested to determine the optimum condition for activity and selectivity i.) the gasoline fraction range of C_5 to C_{11} by wavying the following operating parameters: Space Velocity (SV) (from 500 to 8,000 h^{-1}), reaction temperature (from 260 to 420 °C), MeOH concentration (from 5 to 100%). Relation between physical properties and the catalytic performance of these synthetic catalysts was examined. The results showed that in the suitable range of 3200 to 400, Si/V charged ratio, vanadosilicate catalysts have higher activity and selectivity for MTG than ZSM-5 catalyst.



ACKNOWLEDGEMENT

The author would like to express his sincere gratitude to Assist. Prof Piyasan Praserthdam and Prof. Tomoyuki Inui for their valuable guidance and encouragement to complete this study. He is also deeply grateful to Prof. Ryozo Toei, Prof. Yoshinobu Takegami and Assoc. Prof. Wiwut Tanthapanichakoon for their initiative guidance and helpful into Graduate Research Student Course at the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, during the peroid of this study.

The author wishes to express his sincere gratitude to Ministry of Education of Japan (MONBUSHO) and Div. of Fuel Control, Ministry of Commerce of Thailand for their scholaships. He would like to thank Dr. T. Inoue, Mr. Toshiro Otowa (his tutor), Mr. Takanori Miyake, Mr. Koichi Fukuda, Mr. ... Sakamoto, and Miss T. Ukawa for their help and cooperation to this work.

Finally, the author would like to thank his parents, Mr.Nakorn Medhanavyn and Mrs. Yawamalaya Medhanavyn for their encouragement. He is also grateful to his lover, Miss Kannikar Sungcharoen for her valuable helpful and understanding.

Dhongchai Medhanavyn

January, 1984

TABLE OF CONTENTS



	page
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
TABLE OF CONTENTS.....	vii
LIST OF TABLES.....	x
LIST OF FIGURES.....	xi
NOMENCLATURES.....	xiv
 CHAPTER	
1. INTRODUCTION.....	1
2. CATALYST DESIGN AND PREPARATION.....	4
2.1 Introduction.....	4
2.2 The Design of Catalysts.....	5
2.3 Initial Stage of the Catalyst Design.....	6
2.4 Selection of the Chemical Basis of the Catalyst : Major Catalyst.....	6
2.5 Selection of the Chemical Basis of the Catalyst : Minor components.....	15
2.6 Selection of the Preferred form of the Catalyst	16
2.7 Catalyst Preparation.....	18
2.8 Processing Operations.....	25
3. THE SYNTHESIS AND TOPOLOGY OF ZEOLITE FAMILIES	
3.1 Introduction.....	27
3.2 Topology of the Zeolite Framework.....	29

	page
3.3 Zeolite Synthesis with Organic Reagents.....	39
3.4 Framework Substitutes in Zeolite Synthesis.....	40
4. EXPERIMENTAL METHODS.....	42
4.1 Preparation of Catalysts.....	42
4.2 Reaction Engineering Tests.....	48
4.3 Physical Property Measurements	54
5. RESULTS AND DISCUSSION	59
5.1 Reaction Engineering Tests.....	59
5.2 Physical Propertiy Measurements	75
6. CONCLUSIONS.....	87
REFERENCES.....	89
APPENDIX A	
A-1 Calculation of Tabled Catalyst Volume	91
A-2 Space Velocity Calculation.....	91
A-3 Calculation Yield of Product.....	93
A-4 Vapour Pressure Curve of MeOH at Various Temperature	103
A-5 BET surface area calculation.....	104
A-6 Si/V Charged ratio Calculation	106
A-7 TPD Calculation	106
A-8 Calculation for percentage of MeOH conversion ...	108
A-9 Calculation for C-wt% of dimethyl ether (DME) ...	110
A-10 Calculation for percentage of conversion to hydrocarbons	110

APPENDIX B

B-1 Prepared sample for XRD measurement.....	112
B-2 Method of sample solution preparation for atomic absorption.....	113
APPENDIX C Miscellaneous.....	115
APPENDIX D DATA TABLE	119
VITA.....	128

LIST OF TABLES

	Page
Table 2.1 Summary of adsorption of reactants	13
Table 2.2 Factors that influence support choice	17
Table 2.3 Factors that influence reactor choice	19
Table 2.4 Summary of desired or undesired structures of prepared catalysts	20
Table 3.1 Properties of selected Zeolites and Feldspathoids..	28
Table 5.1 Influence of the Si/V charged ratio on the activity and selectivity of metallosilicate catalysts (at 300° C).....	60
Table 5.2 Influence of the Si/V charged ratio on the activity and selectivity of metallosilicate catalysts (at 360° C).....	63
Table 5.3 The effect of space velocity on activity and selectivity of catalyst H-Si-V (∞ , 400, 200)....	65
Table 5.4 The effect of temperature on activity and selectivity of catalyst H-Si-V (1600).....	68
Table 5.5 The effect of temperature on activity and selectivity of catalyst H-Si-V (90).....	71
Table 5.6 The effect of MeOH concentration on activity and selectivity of catalyst H-Si-V (1600).....	73
Table 5.7 BET surface area of Na-form and H-form vanado- silicate catalysts.....	76
Table 5.8 Atomic absorption analysis of vanadocilicate catalysts.....	78

LIST OF FIGURES

	Page
Figure 2.1 Factors that influence catalyst Selection	6
Figure 2.2 Flow charts summerizing the catalyst design process.....	7
Figure 2.3 Activity pattern for nitrous oxide decomposition....	9
Figure 2.4 Activity pattern for reactions involving hydrogen...	9
Figure 2.5 Activity patterns for oxidation.....	10
Figure 3.1 Three ways of depicting the truncated octahedron (or sodalite unit) in a aluminosilicate framework.....	30
Figure 3.2 Stereodiagram of the framework topology of cancrinite. The dotted line shows one unit cell	31
Figure 3.3 Projections of three-dimensional frameworks of cancrinite and sodalite.....	32
Figure 3.4 Stereodiagram of the framework topology of sodalite.	32
Figure 3.5 Stereodiagram of the framework topology of offretite	33
Figure 3.6 Stereodiagram of the framework topology of gmelinite	33
Figure 3.7 Stereodiagram of the framework topology of chabazite	34
Figure 3.8 Stereodiagram of the framework topology of erionite	34
Figure 3.9 Stereodiagram of the framework topology of type A...	35
Figure 3.10 Stereodiagram of the framework topology of faujasite	36
Figure 3.11 Stereodiagram of the framework topology of ZK-5	37
Figure 3.12 Stereodiagram of the framework topology of mazzite..	37
Figure 3.13 Stereodiagram of the framework topology of type L...	38
Figure 3.14 Stereodiagram of the framework topology of mordenite	39

	Page
Figure 4.1 Preparation method for decant solution and gel precipitate formation.....	43
Figure 4.2 Powder Miller.....	45
Figure 4.3 Flow chart diagram of catalyst preparation by the improved method.....	47
Figure 4.4 Diagram of MTG Reaction Experiment for tube Reactor	
Figure 4.5 Diagram of BET surface area measuring system.....	56
Figure 4.6 Atomic Absorption Equipment.....	58
Figure 4.7 Flow chart of TPD(NH_3) measurement system.....	58
Figure 5.1 Effect of Si/V charged ratio on hydrocarbon distribution at 300° C	61
Figure 5.2 Effect of Si/V charged ratio on hydrocarbon distribution at 360° C	64
Figure 5.3 The effect of space velocity on hydrocarbon distribution.....	66
Figure 5.4 Effect of temperature on hydrocarbon distribution with the catalyst H-Si-V (1600).....	69
Figure 5.5 Effect of temperature on hydrocarbon distribution of the catalyst H-Si-V(90).....	72
Figure 5.6 The effect with the catalyst H-Si-V (1600) distribution of the catalyst H-Si-V (1600).....	74
Figure 5.7 BET surface area curve of Na-form and H-form of vanadosilicate catalysts.....	77
Figure 5.8 A plot of actual Si/V charged ratios vs. theoretical Si/V charged ratios.....	79
Figure 5.9 XRD patterns for vanadosilicate catalysts.....	79
Figure 5.10 TPD(NH_3) curves for vanadocilicate catalysts.....	81

	Page
Figure 5.11 Scanning Electron Micrographs for the Si/V charged ratio ∞	82
Figure 5.12 Scanning Electron Micrographs for the Si/V charged ratio 200.....	83
Figure 5.13 Scanning Electron Micrographs for the Si/V charged ratio 90.....	84
Figure 5.14 Scanning Electron Micrographs for the Si/V charged ratio 40.....	85
Figure A-1 Calibration curve of the micro-speed and mass flow rate of pure MeOH at 0° C.....	92
Figure A-2 The sample peak of catalyst H-Si-V (400) for gasoline analysis.....	94
Figure A-3 Curve of vapour pressure of MeOH related to temperature.....	103
Figure A-4.1 Plot of weight loss vs. time.....	106
Figure A-4.2 Plot of full scale chart related to weight loss vs. speed chart related to time	107
Figure C-1 Skeletal diagram of the (100)- face of the ZSM-5 unit cell.....	115
Figure C-2 Skeletal diagram of the (010)-face of the ZSM-5 unit cell.....	116
Figure C-3 Schematic representation of type A synthesis....	117
Figure C-4 Schematic representation of type B synthesis....	118



NOMENCLATURES

MTG	=	Methanol to gasoline
BET	=	Brunauer Emmett Teller surface area value
TPD(NH ₃)	=	Temperature program of desorption of NH ₃
A.A.	=	Atomic Absorption Analysis
SEM	=	Scanning Electron Microscope
ZSM-5	=	a zeolite catalyst which synthesized by Mobil Oil company (Zeolite socolony of Mobil Oil Co-5)
XRD	=	X-ray Diffraction
M	=	Metal
n	=	number of electrical charge of metal
x	=	stoichiometric number
p	=	vapour pressure of MeOH
A, B, C	=	arbitrary constant of Antonie's equation
t	=	temperature, °C
T	=	location of metal ion in framework crystal
P _o	=	saturated vapor pressure of N ₂
SV	=	space velocity, h ⁻¹
ITG	=	integrating area, unit
DME	=	dimethyl ether
STY _i	=	space time yield of i products.
C ₅ ⁺	=	hydrocarbons which have C-atom ≥ 5 atoms
C ₄ ⁻	=	hydrocarbons which have C-atom ≤ 4 atoms