

**SELECTIVE CATALYTIC REDUCTION OF NO_x BY AMMONIA
USING ITQ-21 CATALYSTS**

Komsit Pinchanchaiyoth

Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University and Institut Français du Pétrole

2006

ISBN 974-9937-45-7

Thesis Title: Selective Catalytic Reduction of NO_x by Ammonia Using ITQ-21 Catalysts
By: Komsit Pinchanchaiyoth
Program: Petroleum Technology
Thesis Advisors: Asst. Prof. Sirirat Jitkarnka
Asst. Prof. Apanee Luengnaruemitchai

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

Nantaya Yanumet
..... College Director
(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

Sirirat Jitkarnka
.....
(Asst. Prof. Sirirat Jitkarnka)

Apanee Luengnaruemitchai
.....
(Asst. Prof. Apanee Luengnaruemitchai)

Pramoch Rangsunvigit
.....
(Assoc. Prof. Pramoch Rangsunvigit)

Kitipat Siemanond
.....
(Asst. Prof. Kitipat Siemanond)

ABSTRACT

4773007063: Petroleum Technology Program

Komsit Pinchanchaiyoth: Selective Catalytic Reduction of NO_x by Ammonia Using ITQ-21 Catalysts.

Thesis Advisors: Asst. Prof. Sirirat Jitkarnka and Asst. Prof. Apanee Luengnaruemitchai 53 pp. ISBN 974-9937-45-7

Keywords: SCR/ NO_x/ ITQ-21/ Mordenite/ NH₃-SCR/ DeNO_x

The synthesis of ITQ-21 was successfully accomplished. 5% ITQ-21 was mixed with H-MOR denoted as 5%ITQ-21/H-MOR. The mixed zeolites with higher acidity than H-MOR due to the addition of ITQ-21 were subsequently used as the support for NO_x reduction. However, the acidity was decreased after the addition of metals. The presence of metals showed enhancement in NO conversion, but it decreased N₂ selectivity. Among the metal-supported H-MOR catalysts, Cu gave the highest NO conversion. ITQ-21 enhanced NO conversion for the metal-containing catalysts by improving the accessibility to the active sites. When compared with all catalysts, Fe/ITQ-21/H-MOR yielded the maximum NO conversion at 400°C. The higher reaction temperature increased NO conversion, depending also on type of metal, but it did not affect on N₂ selectivity. Germanium in ITQ-21 may cause higher acidity of catalysts, resulting in the better N₂ selectivity. In addition, Ge itself was not the appropriate type of deNO_x metal due to its low NO conversion.

บทคัดย่อ

กมลสิทธิ์ ปิ่นชาณชัยยุทธ : การศึกษาปฏิกิริยารีดักชันอย่างเจาะจงของก๊าซไนตริกออกไซด์ด้วยก๊าซแอมโมเนียโดยใช้ซีโอไลต์ชื่อไอทีคิว-21 เป็นตัวเร่งปฏิกิริยา (Selective Catalytic Reduction of NO_x by Ammonia Using ITQ-21 Catalysts) อ. ที่ปรึกษา: ผศ. ดร. ศิริรัตน์ จิตการคำ และ ผศ.ดร.อาภาณี เหลืองนฤมิตชัย 53 หน้า ISBN 974-9937-45-7

การสังเคราะห์ไอทีคิว-21ประสบความสำเร็จ ซึ่ง ได้ถูกผสมกับมอร์เดไนต์ เป็น 5%ITQ-21/H-MOR การใส่ไอทีคิว-21ทำให้มีความเป็นกรดสูงกว่ามอร์เดไนต์ โดยใช้เป็นตัวรองรับตัวเร่งปฏิกิริยาในการลดก๊าซไนตริกออกไซด์ แต่ความเป็นกรดจะลดลงหลังจากใส่โลหะลงไป การใส่โลหะจะเพิ่มความสามารถในการลดก๊าซไนตริกออกไซด์แต่จะลดความเจาะจงในการเกิดก๊าซไนโตรเจน ทองแดงจะมีความสามารถในการลดก๊าซไนตริกออกไซด์สูงสุดในตัวเร่งปฏิกิริยาที่ใช้มอร์เดไนต์เป็นตัวรองรับตัวเร่งปฏิกิริยา การใช้ไอทีคิว-21บนตัวเร่งปฏิกิริยาที่มีโลหะอยู่จะช่วยเพิ่มความสามารถในการลดก๊าซไนตริกออกไซด์ โดยจะเพิ่มความสามารถในการเข้าถึงบริเวณที่ใช้ทำปฏิกิริยาได้ และจากการเปรียบเทียบกับตัวเร่งปฏิกิริยาทั้งหมดพบว่า Fe/ITQ-21/H-MOR จะมีความสามารถสูงที่สุดในการลดก๊าซไนตริกออกไซด์ที่ 400 องศาเซลเซียส อุณหภูมิสูงขึ้นจะช่วยเพิ่มความสามารถในการลดก๊าซไนตริกออกไซด์แต่ก็ขึ้นอยู่กับชนิดของโลหะด้วย เจอมาเนียมในไอทีคิว-21น่าจะเป็นสาเหตุที่ทำให้ตัวเร่งปฏิกิริยามีความเป็นกรดเพิ่มขึ้น และเจอมาเนียมจัดว่าเป็นโลหะที่ไม่เหมาะสมในการลดก๊าซไนตริกออกไซด์ เนื่องจากมีความสามารถในการลดก๊าซไนตริกออกไซด์ต่ำ

ACKNOWLEDGEMENTS

The author gratefully acknowledges Asst. Prof. Sirirat Jitkarnka and Asst. Prof. Apanee Luengnaruemitchai, his advisor and co-advisor, respectively, for their sharp suggestions, discussions, encouragements, and problem solving throughout all course of his work.

The author would like to express his sincere appreciation to Assoc. Prof. Pramoch Rangsunvigit and Asst. Prof. Kitipat Siemanond for serving as his thesis committee.

The author is grateful to PPT consortium for the partial support on his research, and also appreciates the supports from the college staffs.

Finally, the author would like to take this opportunity to thank all his friends at PPC, especially the SJ's group, Petroleum, and also Ph.D. students for their helps.

The author is also greatly indebted to his parents and his family for their support, love and understanding.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	ii
Abstract (in Thai)	iii
Acknowledgements	iv
Table of Contents	v
List of Tables	viii
List of Figures	ix
 CHAPTER	
I INTRODUCTION	1
 II LITERATURE REVIEW	
2.1 NO _x	4
2.2 NO _x Control Technologies	6
2.2.1 Combustion Control	6
2.2.2 Selective Non-Catalytic Reduction (SNCR)	7
2.2.3 Selective Catalytic Reduction (SCR)	7
2.3 Selective Catalytic Reduction of NO _x with NH ₃	8
2.4 Catalysts in SCR Process	9
2.4.1 Vanadium-catalysts	9
2.4.2 Metal-exchanged Zeolite Catalysts	9
2.5 Zeolite	12
2.6 ITQ-21	14

CHAPTER	PAGE	
III	EXPERIMENTAL	17
3.1	Materials and Equipment	17
3.1.1	Chemicals	17
3.1.2	Gases	17
3.1.3	Equipment	18
3.2	Methodology	18
3.2.1	Catalyst Preparation	18
3.2.1.1	N(16)-methylsperminium hydroxide Preparation	19
3.2.1.2	ITQ-21 Synthesis	19
3.2.1.3	Preparation of Metal/ITQ-21/H-MOR Catalysts	19
3.2.1.4	Preparation of Metal/H-MOR Catalysts	20
3.2.1.5	Preparation of 5%Ge/MOR	20
3.2.2	Catalyst Characterization	20
3.2.2.1	Surface Area Measurement (BET)	20
3.2.2.2	X-ray Diffraction (XRD)	20
3.2.2.3	Scanning Electron Microscopy (SEM)	21
3.2.2.4	Transmission Electron Microscope (TEM)	21
3.2.2.5	Temperature Programmed Desorption of Ammonia (NH ₃ -TPD)	21
3.2.3	Catalytic Activity Measurements	21
IV	RESULTS AND DISCUSSION	22
4.1	Catalyst Preparation	22
4.1.1	ITQ-21 Synthesis	22
4.2	Catalyst Characterization	24

CHAPTER	PAGE
4.2.1 Scanning Electron Microscope (SEM)	24
4.2.2 Transmission Electron Microscope (TEM)	24
4.2.3 Surface Area Measurement (BET)	25
4.2.4 Temperature Programmed Desorption of Ammonia (NH ₃ -TPD)	26
4.2.4.1 Effect of Metals on Acid Properties	26
4.2.4.2 Effect of ITQ-21 on Acid Properties	29
4.3 Catalytic Activity Measurements	30
4.3.1 Effect of The Addition of Metals on SCR Activity	30
4.3.2 Effect of ITQ-21 on SCR Activity	33
4.3.3 Effect of Metals on SCR Activity	35
4.3.4 Effect of Reaction Temperature on SCR Activity	36
4.3.5 Effect of The Presence of Germanium on SCR Activity	38
4.3.6 Reaction Pathways on SCR Activity	39
V CONCLUSIONS AND RECOMMENDATIONS	41
REFERENCES	42
APPENDICES	46
Appendix A Calculation of NO Conversion and N ₂ /N ₂ O Selectivity	46
Appendix B Raw Data	48
Appendix C Metal Crystal Size Calculation from XRD	52
CURRICULUM VITAE	53

LIST OF TABLES

TABLE		PAGE
2.1	Summary of NO and NO ₂ formation	5
2.2	Emission standards for municipal waste incinerators	6
2.3	Relative acidity of zeolites as determined by pyridine adsorption-desorption experiment	16
4.1	Suitable conditions for ITQ-21 synthesis	22

LIST OF FIGURES

FIGURE	PAGE
2.1 Simplified SCR chemistry	8
2.2 Some types of well-known zeolites	13
2.3 Perspective view of the unit cell of ITQ-21	15
4.1 Diffractograms of ITQ-21 obtained from: (a) Synthesis using the conditions in Table 4.1, and (b) from the literature	23
4.2 XRD pattern of the synthesized ITQ-21 (Top) in comparison with that from the literature (Bottom)	24
4.3 SEM micrographs of ITQ-21 catalyst at different magnifications: (a) 1,000 X, and (b) 10,000 X	25
4.4 TEM micrographs of ITQ-21 catalyst at different magnifications: (a) 85,000 X, and (b) 150,000 X	25
4.5 NH ₃ -TPD profiles of the catalysts with and without metal loading: (a) on the H-MOR support, and (b) on the ITQ-21/H-MOR support.	26
4.6 Comparison in acidity of the catalysts with and without metal loading: (a) on the H-MOR support and (b) on the ITQ-21/H-MOR support	27
4.7 Comparison in acid strength of the catalysts with and without metal loading: (a) on the H-MOR support, and (b) on the ITQ-21/H-MOR support	28
4.8 Effect of ITQ-21 addition into H-MOR on Acidity	29
4.9 Effect of ITQ-21 addition into H-MOR on Acid Strength	30
4.10 NO conversion of catalysts with and without metal loading: (a) on the ITQ-21/H-MOR support, and (b) on the MOR support	31

FIGURE	PAGE
4.11 N ₂ /N ₂ O selectivity of catalysts with and without metal loading: (a) on the ITQ-21/H-MOR support, and (b) on the MOR support	32
4.12 NO conversion of (a) Fe-loaded, (b) Cu-loaded, (c) Co-loaded, (d) Ni-loaded, and (e) unloaded catalysts on both H-MOR and ITQ-21/H-MOR supports	33
4.13 N ₂ /N ₂ O selectivity of (a) Fe-loaded, (b) Cu-loaded, (c) Co-loaded, (d) Ni-loaded, and (e) unloaded catalysts on both H-MOR and ITQ-21/H-MOR supports	34
4.14 NO conversion on the catalysts promoted with different metals and supports: (a) H-MOR, and (b) ITQ-21/H-MOR support	35
4.15 N ₂ /N ₂ O selectivity on the catalysts promoted with different metals and supports: (a) H-MOR, and (b) ITQ-21/H-MOR support	36
4.16 NO conversion of all catalysts at different temperatures: (a) 250°C, (b) 300°C, (c) 350 °C, and (d) 400°C	37
4.17 N ₂ /N ₂ O selectivity of all catalysts at different temperatures: (a) 250°C, (b) 300°C, (c) 350 °C, and (d) 400°C	37
4.18 Effect of germanium in the framework on (a) NO conversion, and (b) N ₂ /N ₂ O selectivity	38
4.19 Effect of germanium as a metal on: (a) NO conversion, and (b) N ₂ /N ₂ O selectivity	39
4.20 NO _x reduction mechanism	39
C1 Crystal size of reduced metals calculated from XRD	52