

**DEVELOPMENT OF POLYANILINE/ZEOLITE COMPOSITES AS
A CO/N₂ SENSOR**



Ms. Nataporn Densakulprasert

A 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,
and Case Western Reserve University

2003

ISBN 974-17-2329-6

Thesis Title: Development of Polyaniline/Zeolite Composites as a
CO/N₂ Sensor
By: Nataporn Desakulprasert
Program: Polymer Science
Thesis Advisors: Assoc. Prof. Anuvat Sirivat
Prof. Johannes W. Schwank

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

K. Bunyakiat
..... College Director
(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

Anuvat Sirivat
.....
(Assoc. Prof. Anuvat Sirivat)

Johannes Schwank
.....
(Prof. Johannes Schwank)

Sujitra Wongkasemjit
.....
(Assoc. Prof. Sujitra Wongkasemjit)

Ratana Rujiravanit
.....
(Asst. Prof. Ratana Rujiravanit)

ABSTRACT

4472010063 : POLYMER SCIENCE PROGRAM

Nataporn Densakulprasert: Development of Polyaniline/Zeolite
Composites as CO/N₂ Sensor

Thesis Advisors: Assoc. Prof. Anuvat Sirivat and

Prof. Johannes W. Schwank xx pp. ISBN 974-17-2329-x

Keywords : Polyaniline/CO sensor/Conductive Polymer/Zeolite Y,
Zeolite 13X, AIMCM41

Polyaniline (PANI) is one of the most popular conductive polymers used for sensor applications due to the ease of synthesis, and environmental and thermal stability. Zeolite with gas adsorptivity is utilized to composite with polyaniline doped Maleic acid, in order to increase the sensor sensitivity. In this study, we used zeolite Y, 13X and AIMCM41 with the pore sizes of 7, 10, 36 Å, and the Cu²⁺ exchange capacity of 0.32, 0.17 and 0.087 mol/g, respectively. The sensor sensitivity found to be increased with the zeolite content. To study the effect of zeolite types, the content of 10%wt was selected because of its moderate sensitivity and processibility. We found that the highest sensitivity was provided by the composite of zeolite 13x, followed by zeolite Y, and AIMCM 41, respectively. The lower in sensitivity of zeolite Y is due to the excess of Cu²⁺ ions that is reduced free volume of zeolite to absorb CO molecules. The too large pores size with less amount of Cu²⁺ in AIMCM41 is not effective to absorb CO molecules.

บทคัดย่อ

นักพร เค้นสกุลประเสริฐ: การปรับปรุงความสามารถในการตรวจวัดปริมาณคาร์บอนมอนอกไซด์ในไนโตรเจนก๊าซของพอลิอะนิลีนโดยการผสมกับซีโอไลต์ (Development of Polyaniline/Zeolite Composites as a CO_{N₂} Sensor) อ.ที่ปรึกษา: รศ.ดร.อนุวัฒน์ ศิริวัฒน์ และศ. ดร.โจฮานเนส ดับบลิว ชเวกซ์ xx หน้า ISBN 974-17-2329-x

พอลิอะนิลีนเป็นพอลิเมอร์นำไฟฟ้า สามารถนำมาประยุกต์ใช้ในการตรวจวัดปริมาณคาร์บอนมอนอกไซด์ก๊าซ เนื่องด้วยข้อจำกัดประสิทธิภาพของพอลิอะนิลีนในการตรวจวัดก๊าซที่มีความเข้มข้นต่ำๆ ซีโอไลต์เป็นสารที่มีโครงสร้างเป็นรูพรุนมีความสามารถในการดูดซับโมเลกุลต่างๆ จึงถูกนำมาผสมกับพอลิอะนิลีน ซีโอไลต์ Y, 13X และ AIMCM41 มีคุณสมบัติแตกต่างกันทั้งขนาดรูพรุนและปริมาณคอปเปอร์ไอออนถูกเลือกมาผสมกับพอลิอะนิลีนที่ผ่านการได้ปด้วยกรดมาเลอิกเพื่อศึกษาผลกระทบของปริมาณซีโอไลต์ในตัวอย่าง และชนิดของซีโอไลต์ที่มีผลต่อประสิทธิภาพการตรวจวัดก๊าซปริมาณคาร์บอนมอนอกไซด์ จากการศึกษาพบว่า การเพิ่มปริมาณปริมาณซีโอไลต์ช่วยเพิ่มประสิทธิภาพของตัวอย่างในการตอบสนองต่อคาร์บอนมอนอกไซด์ก๊าซ และจากการศึกษาชนิดของซีโอไลต์ พบว่าตัวอย่างผสมระหว่างพอลิอะนิลีนกับซีโอไลต์ 13X ให้ประสิทธิภาพต่อการตรวจวัดก๊าซปริมาณคาร์บอนมอนอกไซด์ดีที่สุด ส่วนตัวอย่างผสมระหว่างพอลิอะนิลีนกับซีโอไลต์ AIMCM41 ให้ผลไม่แตกต่างจากตัวอย่างพอลิอะนิลีนบริสุทธิ์มากนัก

ACKNOWLEDGEMENTS

The author would like to thank all faculties who have provided invaluable knowledge to her, especially, Assoc. Prof. Anuvat Sirivat who is her advisor.

Special thank Ms. Ladawan Ruangchuay for her various discussions and suggestions on this work.

She would like to thank Mr Wanchai Lerdwijitjarud, Ms Datchanee Chotpattananont and Ms Siriluk Suksamranchit for the encouragement and the suggestions on the oral presentations.

She would like to thank C.P.O. Poon Arjpru for his hard works in maintenance the conductive meter, and in addition for taking care of her health for all year.

This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

Finally, the sincerest appreciation is for her family for the love, understanding, encouragement, and financial support.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	xi
 CHAPTER	
I INTRODUCTION	1
1.1 Conductive Polymer	2
1.2 Polyaniline	3
1.3 Zeolite	5
 II LITERATURE SURVEY	 7
2.1 Polyaniline and Doped Polyaniline	7
2.2 Polyaniline as Gas Sensor	8
2.3 Zeolite	9
 III EXPERIMENTAL	 12
3.1 Materials	12
3.2 Methodology	12
3.2.1 Preparation of Polyaniline	12
3.2.2 Preparation of Zeolite	14
3.2.3 Composite Preparation	17
3.2.4 Characterization	17
3.2.5 Conductivity Measurement: Four-point Probe Meter	19

CHAPTER	PAGE
IV Polyaniline/Zeolite Composites as CO/N₂ Sensors	24
1. Introduction	25
2. Experimental	26
3. Results and Discussion	30
4. Conclusions	33
5. Acknowledgements	34
V CONCLUSIONS	44
REFERENCES	46
APPENDICES	
Appendix A FT-IR spectrum of emeraldine base and doped polyaniline	49
Appendix B The TGA thermogram of emeraldine base and doped polyaniline	51
Appendix C Calculate the percent doping level of doped polyaniline by FT-IR	54
Appendix D Calculation of doping level using elemental analysis	56
Appendix E Determination of the crystallinity of PANI and doped PANI	58
Appendix F Characterization of AlMCM41 and zeolite Y and 13X using X-ray diffraction	60
Appendix G Determination of the Cu ²⁺ exchange capacity of zeolite Y, 13X, and AlMCM41 using X-ray fluorescence	62

CHAPTER		PAGE
Appendix H	Determination of pore size and surface area of AlMCM41 and Zeolite Y and 13X using BET	63
Appendix I	Determination of particle sizes of zeolite Y, 13X and AlMCM41 by particle size analyzer	64
Appendix J	Scanning electron micrograph of PANI, doped PANI, and zeolites	68
Appendix K	Determination of the correction factor	74
Appendix L	Determination of Ohmic regime	79
Appendix M	Sensitivity measurement	84
CURRICULUM VITAE		92

LIST OF TABLES

TABLE		PAGE
CHAPTER I		
1.1	The guide line value for common pollutants	1
CHAPTER IV		
1	Summary of zeolite properties	35
2	The conductivity, sensitivity and concentration dependence of composites	35
APPENDICES		
A1	The FT-IR absorption spectrum of polyaniline and doped polyaniline with HCl, MA, and CSA.	50
B1	The percent weight loss of emeraldine base and doped PANI	51
C1	Summary of the percent doping level of PANI-HCl, PANI-MA, and PANI-CSA	55
D1	Calculation of doping level from elemental analysis	57
D2	Raw data from elemental analysis	57
E1	Values of 2θ , d-spacing (\AA) and Miller indices of emeraldine hydrochloride	58
E2	Calculated crystallinity of PANI and doped PANI with HCl, MA, and CSA	59
G1	The element content in zeolite Y, 13X, and AlMCM41 determined using X-ray fluorescence	62
H1	Area-volume-pore size summary from BET	63
I1	Summarized the particle diameter and specific surface area of PANI, doped-PANI, Zeolite Y, 13X and Al MCM41	64
I2	Raw data from particle size analysis of Zeolite Y	65
I3	Raw data from particle size analysis of Zeolite 13X	66

TABLE		PAGE
I3	Raw data from particle size analysis of Zeolite AIMCM41	67
K1	Determination the correction factor of probe A and B	76
K2	Determination the correction factor of probe A with standard Si wafer (specific resistivity 0.014265 Ω .cm, thickness 0.0724 cm.)	78
K3	Determination the correction factor of probe B with standard Si wafer (specific resistivity 0.014265 Ω .cm, thickness 0.0724 cm.)	78
L1	The raw data of the determination of linear regime of doped PANI	80
M1	The conductivity response of PANI-1MA exposed to CO/N ₂ gas	85
M2	The conductivity response of PANI-10MA exposed to CO/N ₂ gas	86
M3	The conductivity response of PANI-10MA/10-13X exposed to CO/N ₂ gas	87
M4	The conductivity response of PANI-10MA/20-13X exposed to CO/N ₂ gas	88
M5	The conductivity response of PANI-10MA/40-13X exposed to CO/N ₂ gas	89
M6	The conductivity response of PANI-10MA/10/Y exposed to CO/N ₂ gas	90
M7	The conductivity response of PANI-10MA/10-MCM41 exposed to CO/N ₂ gas	91

LIST OF FIGURES

FIGURE	PAGE
CHAPTER I	
1.1	3
1.2	4
1.3	5
1.4	5
<p style="margin-left: 20px;">a) Tetrahedral structure $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$, b) sodalite cage, and c) Framework Zeolite Y.</p>	
CHAPTER III	
3.1	16
3.2	17
3.3	22
CHAPTER IV	
1	36
<p style="margin-left: 20px;">The SEM morphology with 20 kV and magnification 2000 of a) PANI-MA, b) Zeolite Y, c) Zeolite 13X, and d) AIMCM41</p>	
2	37
<p style="margin-left: 20px;">The SEM morphology of pellet sample with 25 kV and magnification 2000 of a) PANI-10MA, b) PANI-10MA/10-Y, c) PANI-10MA/10-13X, and d) PANI-10MA/10-AIMCM41.</p>	
3	38
<p style="margin-left: 20px;">The electrical response of the PANI-10MA/10_13X to CO at 1000 ppm, at 1 atm humidity 54-67% and temperature 30 ± 2 °C.</p>	
4	39
<p style="margin-left: 20px;">Proposed mechanism of CO-PANI interaction</p>	
5	40
<p style="margin-left: 20px;">$\Delta\sigma/\sigma$ vs.the [CO] of PANI-MA, PANI-MA/10_13X, PANI-MA/20_13X, and PANI-MA/40_13X at 1 atm, humidity 54-67%, and temperature 30 ± 2OC</p>	

FIGURE	PAGE
6 $\Delta\sigma/\sigma$ vs.the [CO] of PANI-MA, PANI-MA/10_13X, PANI-MA/10_Y, and PANI-MA/10_AIMCM41 at 1 atm, humidity 54-67%, and temperature 30 ± 2 °C	41

APPENDICES

A1 The FT-IR spectrum of PANI doped with HCl, MA, and CSA with $N_A/N_{EB} = 10$.	49
B1 The TGA thermogram of polyaniline doped with HCl.	52
B2 The TGA thermogram of polyaniline doped with MA.	52
B3 The TGA thermogram of polyaniline doped with CSA.	53
E1 X-ray pattern of PANI and doped PANI with $N_A/N_{EB} = 10$.	59
F1 XRD pattern of Cu^{2+} -zeolite Y.	61
F2 XRD pattern of Cu^{2+} zeolite 13X.	61
F3 XRD pattern of Cu^{2+} zeolite AIMCM41.	62
I1 Particle diameters of the Y, 13X and AIMCM41 zeolites.	64
J1 The morphology of polyaniline emeraldine base powder at magnification 2000.	
J2 The morphology of polyaniline powder doped with HCl at magnification 2000 a) PANI-1HCl and b) PANI-HCl.	68
J3 The morphology of polyaniline powder doped with MA at magnification 2000 a) PANI-1MA and b) PANI-MA.	69
J4 The morphology of polyaniline powder doped with CSA at magnification 2000 a) PANI-1CSA and b) PANI-CSA.	69
J5 The morphology of Cu^{2+} Zeolite Y powder a) x2000 and b) x7500.	70
J6 The morphology of Cu^{2+} Zeolite 13X powder a) x2000 and b) x7500.	70
J7 The morphology of Cu^{2+} AIMCM41 powder a) x2000	

	b) x5000, and c) x20000.	71
J8	The morphology of PANI and PANI composite with zeolite 13X at magnification 2000 a) PANI-10MA, b) PANI-10MA/10-13X, c) PANI-10MA/20-13X, and d) PANI-10MA/40-13X.	72
J9	The morphology of PANI composite with zeolite Y and AlMCM41 at magnification 2000 a) PANI-10MA/10-Y and b) PANI-10MA/10-AlMCM41.	73
K1	Linear four-point probe array.	73
L1	Linear regime of PANI doped maleic acid with $N_A/N_{EB} = 1$ and 10	79