ต้นฉบับ หน้าขาดหาย

DEVELOPMENT OF POLYANILINE/ZEOLITE A COMPOSITE AS A **CARBONMONOXIDE SENSOR**

Ms. Chintana Chuapradit

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 2002 ISBN 974-03-1610-7



Thesis Title : Development of Polyaniline/Zeolite A Composite as a

Carbonmonoxide Sensor

By : Ms. Chintana Chuapradit

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.

(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

(Assoc. Prof. Anuvat Sirivat)

(Prof Johannes W. Schwank)

(Assoc. Prof. Sujitra Wongkasemjit)

Rathanaun Hagriagne

(Asst. Prof. Rathanawan Magaraphan)

บทคัดย่อ

จินตนา เชื้อประดิษฐ์: การพัฒนาสารประกอบพอลิอะนิลินกับซีโอไลท์เอสำหรับตรวจ จับก๊าชคาร์บอนมอนอไซด์ (Development of Polyaniline/Zeolite A Composite as a Carbonmonoxide Sensor) อ.ที่ปรึกษา: ศ. คร.โจฮานเนส คับบลิว ชแวงค์และรศ.คร.อนุวัฒน์ ศิ ริวัฒน์ 123 หน้า ISBN 974-03-1610-7

พอลิอะนิลีนเป็นพอลิเมอร์นำไฟฟ้าที่มีการใช้งานอย่างแพร่หลายเนื่องจากคุณสมบัติที่ดี ตัวอย่างเช่นง่ายต่อการสังเคราะห์ แต่เมื่อนำพอลิอะนิลีนมาใช้เป็นตัวตรวจสอบก๊าซพบว่าพอลิอะ นิลีนมีความเฉพาะต่อการตรวจสอบชนิดของก๊าซต่ำ ซีโอไลท์ชนิดเอเป็นตัวดูดซับที่มีโครงสร้าง เป็นรูพรุนขนาดเล็กระดับไมครอนที่ซึ่งมีคุณสมบัติในการเลือกดูดซับต่อชนิดของสารที่ถูกดูดซับ บนพื้นฐานของความแตกต่างในระดับโครงสร้างที่เป็นรูพรุนและความเป็นขั้ว ซีโอไลท์เอ 3 ชนิด ถูกเลือกมาบคผสมกับพอลิอะนิลีน เพื่อทำสารประกอบพอลิอะนิลีนซีโอไลท์โดยศึกษาผลกระทบ ที่เกิดจากชนิดของกรดที่เป็นตัวโด๊ป ความเข้มข้นของตัวโด๊ป ชนิดของซีโอไลท์และปริมาณของ ซีโอไลท์ในสารประกอบพอลิอะนิลีนซีโอไลท์เอ ในการตอบสนองทางไฟฟ้าต่อก๊าซคาร์บอนมอ นอไซค์ของสารประกอบคั้งกล่าว จากการศึกษาพบว่ากรคไฮโครคลอริกให้ระดับการโค๊ปสูงกว่า กรคมาเลอิกที่อัตราส่วนโคยมวลระหว่างกรคกับพอลิอะนิลินต่ำกว่า 2 เท่า และการนำไฟฟ้าของ พอลิอะนิลีนเพิ่มขึ้นอย่างรวดเร็วตามระดับการโด๊ปที่เพิ่มขึ้น เมื่ออัตราส่วนโดยมวลของกรดต่อ พอลิอะนิลีนสูงขึ้น เปอร์เซนต์โด๊ปของพอลิอะนิลีนเข้าสู่สมคุลที่ 100% ซึ่งให้ค่าการนำไฟฟ้า ประมาณ 4 ซึเมนท์ต่อเซนติเมตร ความไวในการตอบสนองของพอลิอะนิลีนต่อความเข้มข้นของ ก๊าซคาร์บอนมอนอไซต์มีความสัมพันธ์กันตามสมการยกกำลัง ที่ซึ่งพอลิอะนิลีนโด๊ปด้วยกรดมา เลอิกที่อัตราส่วนโดยมวลเท่ากับ10 เหมาะต่อการใช้ตรวจสอบปริมาณก๊าซคาร์บอนมอนอกไซด์ เพราะแสดงค่าการนำไฟฟ้าและความว่องไวในการตอบสนองสูง สำหรับการตอบสนองต่อก๊าซ คาร์บอนมอนอกไซต์ของสารประกอบพอลิอะนิลีนซีโอไลท์เอนั้นพบว่าสารประกอบพอลิอะนิลีน ซีโอไลท์เอมีค่าความว่องไวในการตอบสนองลคลงเมื่อเปรียบเทียบกับพอลิอะนิลีนทั้งนี้เพราะการ ลดลงของปริมาณพอลิอะนิลีน

ABSTRACT

4372007063 : POLYMER SCIENCE PROGRAM

Chintana Chuapradit: Development of Polyaniline/Zeolite

A Composite as a Carbonmonoxide Sensor

Thesis Advisors: Prof. Johannes W. Schwank and

Assoc. Prof. Anuvat Sirivat, 123 pp. ISBN 974-03-1610-7

Keywords : Polyaniline/CO sensor/Conductive Polymer/Zeolite A

Polyaniline (PANI) is one of the most promising conductive polymers. Despite all the advantages of polyaniline, such as its ease of synthesis, polyaniline has low selectivity when it is used as a gas sensor. Three types of zeolite LTA: KA, NaA and CaA, were chosen based on different effective pore size and polarity, and mixed with maleic acid MA-doped PANI (PANI-MA) in a dry mixing process to produce PANI/Zeolite A. The effects of acid dopant type, dopant concentration, zeolite type and zeolite A content on electrical conductivity responses when exposed to CO at room temperature are studied. At acid-aniline monomer mole ratio $N_A/N_{\rm EB}$ less than 2.0, HCl-doped polyaniline had a higher doping level than MA-doped polyaniline where the electrical conductivity increased dramatically with doping level. At acid-aniline monomer mole ratios greater 2.0, the doping levels and σ reached equilibrium values of ~ 100% and 4 S/cm, respectively. The CO sensitivity of the polyaniline sensor was found to obey the power law $\Delta \sigma = a [CO]^b$, b ~0.35-0.75. PANI-10.0MA is suitable for use as a CO sensor because it has a high conductivity and sensitivity. The PANI-10MA/Zeolite A sensor had lower CO gas sensitivity than pure PANI-10MA. All zeolites A type reduced the CO gas sensitivity of the PANI-10MA sensor because of the decrease of PANI-10MA free volume.

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.

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

Special thank is extended to her entire friends for their helps and suggestions, especially, Ms. Sutthida Watcharaphalakorn.

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 also thanks Mr. Srichalai Khunthon who operated ball mill. In addition, she would like to thank all the College members, and staff of the Petroleum and Petrochemical College, Chulalongkorn University for valuable equipment, instrument training both in theory and practice.

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

TABLE OF CONTENTS

				PAGE
	Title F	Page		i
	Abstra	act (in English)		iii
	Abstra	act (in Thai)		iv
	Ackno	owledgements		V
	Table	of Contents		vi
	List of	f Tables		ix
	List of	f Figures		xii
	List of	f Schemes		xv
CHAP'	ΓER			
	I	INTRODUCTION		1
		1.1 Introduction		1
		1.2 Background		2
		1.3 Objectives		7
	II	LITERATURE SURVEY		
		2.1 Synthesis of Polyaniline		8
		2.2 Acid Doped Polyaniline		8
		2.3 Polyaniline as Gas Sensors		10
		2.4 Zeolite and Polyaniline/Zeolite A Composite		11
	III	EXPERIMENTAL		13
		3.1 Materials		13
		3.2 Methodology	_	13
		3.2.1 Purification of Aniline Monomer		14
		3.2.2 Synthesis of Polyaniline Base		14
		3.2.3 Preparation of Doped Polyaniline Powder		15
		3.2.4 Preparation of Doped Polyaniline Pellet		15
		3.2.5 Composite Preparation		16

	3.2.6 Characterization	16
	3.2.7 Conductivity Measurement	18
	3.2.8 Gas Measurement	19
IV	RESULTS AND DISCUSSION	20
	4.1 Polyaniline	20
	4.1.1. Synthesized Polyaniline Characterization	20
	4.1.2. Acid-Doped Polyaniline Characterization	22
	4.1.3 Conductivity of Acid-Doped Polyaniline	37
	4.1.4 Sensitivity and Interaction of Acid-Doped	42
	Polyaniline to CO	
	4.2 Polyaniline/Zeolite Composite	49
	4.2.1 Zeolite Characterization	49
	4.2.2 Polyaniline/Zeolite A Composite Characterization	51
	4.2.3 Conductivity of PANI/Zeolite 4A Composite	53
	4.2.4 Sensitivity of PANI-10MA/Zeolite A Composite	53
	on CO Exposure	
V	CONCLUSIONS	58
	REFERENCES	59
	APPENDICES	63
	Appendix A Elemental analysis data	63
	Appendix B FT-IR measurement	67
	Appendix C XRD measurement	70
	Appendix D TGA measurement	74
	Appendix E SEM measurement	83
	Appendix F Particle size data	88
	Appendix G Determination of Ohmic's law regime	95
	Appendix H Determination of the geometric	98
	correction factor	

Appendix I Conductivity measurement	101
Appendix J Sensitivity measurement ($\Delta \sigma$)	110
CURRICULUM VITAE	123

LIST OF TABLES

TABLE		PAGE
4.1	Function group of synthesized polyaniline emeraldine base	21
4.2	TGA result of EB and acid doped polyaniline	23
4.3	Doping level of PANI-HCl and PANI-MA powder	25
4.4	Summarized FT-IR peaks of emeraldine base	28
	and acid-doped polyaniline	
4.5	Doping level of PANI-HCl by FT-IR technique	29
4.6	Crystallinity and doping level of PANI-HCl and PANI-MA	34
4.7	Characteristic of acid doped polyaniline pellet	46
4.8	Scaling exponent, scaling prefactor, and	49
	conductivity of all acid doped polyanilines	
4.9	Window size diameter of zeolite A powder	50
	at different cation	
4.10	The %weight loss of zeolite A powder	50
	at different window sizes	
4.11	Average particle size of zeolite A powder	50
	at different window size diameter	
4.12	Scaling exponent and scaling prefactor of	55
	PANI-10MA/Zeolite 4A composite	
4.13	Scaling exponent and scaling prefactor of	57
	PANI-10MA/20Zeolite A composite with	
	different zeolite window size.	
A1	Raw data and calculated data of acid doped polyaniline	63
A2	Mole ratio of each element of PANI-HCl powder	65
A3	Chemical structure of PANI-HCl powder and %doping level	65
A4	Mole ratio of each element of PANI-MA powder	66
A5	Chemical structure of PANI-HCl powder and %doping level	66

B1	Raw data of %absorbence area and %apparent doping	69
	level of PANI-HCl	
C1	Crystallinity of PANI-HCl	71
C2	Crystallinity of PANI-MA	72
C3	Relationship between specific conductivity and	73
	crystallinity of PANI-HCl	
C4	Relationship between specific conductivity and	73
	crystallinity of PANI-MA	
D1	TGA data of PANI-HCI	75
D2	TGA data of PANI-MA	77
D3	Percentage of weight loss and onset temperature of PANI-HCl	79
D4	Percentage of weight loss and onset temperature of PANI-MA	79
D5	TGA data of eeolite A after dried at 120°C ~6h	80
D6	Percentage of weight loss and onset temperature	82
	of zeolite A powder	
F1	Raw data of agglomerate particle size of polyaniline powder	89
F2	Raw data of agglomerate particle size of zeolite 3A powder	91
F3	Raw data of agglomerate particle size of zeolite 3A powder	92
F4	Raw data of agglomerate particle size of zeolite 5A powder	93
G1	Raw data of determination of linear regime of Silicon Wafer	96
G2	Raw data of determination of linear regime of polyaniline	97
H1	Sheet resistivity and thickness of standard sheet (SiO)	99
H2	Determination of K factor	100
I1	Raw data of conductivity measurement of PANI-HCl in air	102
I2	Raw data of conductivity measurement of PANI-MA in air	105
I3	Raw data of conductivity measurement of PANI-10MA	108
	/Zeolite 4A composite in air	
J1	Sensitivity measurement data of PANI-1HCl	111
J2	Sensitivity measurement data of PANI-10HCl	112
J3	Sensitivity measurement data of PANI-1MA	114
J4	Sensitivity measurement data of PANI-10MA	115

J5	Sensitivity measurement data of PANI-10MA/10Zeolite 4A	117
J6	Sensitivity measurement data of PANI-10MA/20Zeolite 4A	118
J7	Sensitivity measurement data of PANI-10MA/40Zeolite 4A	119
Ј8	Sensitivity measurement data of PANI-10MA/20Zeolite 3A	120
19	Sensitivity measurement data of PANI-10MA/20Zeolite 5A	121

LIST OF FIGURES

FIGURE		PAGE
4.1	TGA thermograms of polyaniline emeraldine base	20
	under nitrogen atmosphere	
4.2	FT-IR spectrum of synthesized polyaniline emeraldine	21
	base	
4.3	UV-VIS spectrum of synthesized polyaniline emeraldine	22
	base in NMP solvent	
4.4	TGA thermograms of (a) an emeraldine base,	23
	(b) HCl-doped polyaniline, (PANI-HCl) and (c) MA-doped	
	polyaniline, (PANI-MA) at doping ratios = 1.0	
4.5	Moisture content of PANI-HCl and PANI-MA powder	24
	at various doping ratios	
4.6	Relation between %doping level of PANI-HCl and	26
	PANI-MA powder and acid-emeraldine base mole ratio.	
4.7	FT-IR spectrum of PANI-HCl at various doping ratios	27
4.8	FT-IR spectrum of PANI-MA at various doping ratios	27
4.9	Relation between %doping level of of PANI-HCl	30
	and acid-emeraldine base mole ratio by FT-IR measurement	
4.10	UV-Visible spectrum of PANI-HCl solution	31
	in NMP at various doping ratios	
4.11	UV-Visible spectrum of PANI-MA solution	32
	in NMP at various doping ratios	
4.12	XRD pattern of polyaniline emeraldine base and	33
	PANI-HCl in pellet form at various doping ratios	
4.13	XRD pattern of polyaniline emeraldine base and	33
	PANI-MA in pellet form at various doping ratios	
4.14	Relation between crystallinity structure and doping level	35
4.15	Morphological structure of PANI-HCl	36
	at various doping ratios	

4.16	Morphological structure of PANI-MA at various doping ratios	36
4.17	Effect of the doping level on the specific conductivity	38
	as determined by EA technique	
4.18	Conductivity/%doping level as a function of %crystallinity	39
4.19	Effects of vacuum, and carbon monoxide on	41
	the specific conductivity of acid doped polyaniline pellet	
	at 27-28°C and 65-69% relative humidity	
4.20	FT-IR spectra of PANI-HCl before and	43
	In-situ exposure to 1000 ppm CO/N ₂ mixture:	
4.21	XRD pattern of PANI-HCl before and after exposed to CO	44
4.22	XRD pattern of PANI-MA before and after exposed to CO	45
4.23	Response of PANI-HCl to different CO/N2 concentration	46
	at 27-28°C and 65-69% relative humidity	
4.24	Response of PANI-MA to different CO/N2 concentration	47
	at 27-28°C and 65-69% relative humidity	
4.25	Thermogram of zeolite A powder	51
4.26	Particle size distribution of zeolite 4A powder	52
4.27	Morphology of zeolite A powders at different	52
	molecular structure (x2000): (a) Zeolite NaKA, (3A),	
	(a) Zeolite NaA, (3A), and (c) Zeolite NaCaA, (3A)	
4.28	Morphology of Polyaniline/Zeolite NaA composite	53
	at different zeolite content (x1000)	
4.29	Effect of zeolite 4A on specific conductivity of	54
	polyaniline pellet	
4.30	Relation between $\Delta\sigma$ and CO concentration of	55
	PANI-10MA/Zeolite A composite at 20% zeolite content	
	in 1 atm, 27-28°C and 65-69% relative humidity	
4.31	Relation between $\Delta\sigma$ and CO concentration of	56
	PANI-10MA/Zeolite A composite at 20% zeolite content	
	in 1 atm, 27-28°C and 65-69% relative humidity	

E1	Morphology of polyaniline powders after doping	83
	with HCl at various N _A /N _{EB}	
E2	Morphology of polyaniline powders after doping with	84
	MA at various N _A /N _{EB}	
E3	Morphology of zeolite A powders at different molecular	85
	structure	
E4	Morphological structure of PANI-HCl pellet	86
	at (a) $N_A/N_{EB} = 1.0$ and (b) $N_A/N_{EB} = 10.0$	
E5	Morphological structure of PANI-MA pellet	86
	at (a) $N_A/N_{EB} = 1.0$ and (b) $N_A/N_{EB} = 10.0$	
E6	Morphological structure of PANI-10MA,	87
	zeolite 4A and PANI-10MA/Zeolite4A	
	at various zeolite contents (x1000)	
F1	Particle size distribution of polyaniline powder	90
F2	Particle size distribution of zeolite A powder	94
G1	Ohmic's law region of the silicon wafer Si 10-28A	95
G2	Ohmic's law region of PANI-10HCl and PANI-10MA	96

LIST OF SCHEMES

SCHEME		PAGE
1.1	Zeolite structure	6
3.1	Conductivity detectors with gas chamber	19
4.1	Pseudo-orthorombic unit cell of acid doped polyaniline	34
4.2	Schematic representation of the inhomogeneous	41
	metalic island model.	
4.3	Interaction between CO and the conductive polyaniline	43
C1	Integral area of the diffraction patterns of acid-doped	70
	polyaniline	
HI	Linear array four-point probe meter	98