

Copyright by
Yashan Zhang

2013

APPROVAL PAGE

Doctor of Philosophy Dissertation

**Layered Rare Earth and Transition Metal Materials: Synthesis,
Modification and Catalytic Application**

Presented by

Yashan Zhang, B.E. & B.A.

Major Advisor _____

Steven L. Suib

Associate Advisor _____

Prabhakar Singh

Associate Advisor _____

Alfredo Angeles-Boza

University of Connecticut

2013

Dedicated to April and Le Petit Pipiniu

ACKNOWLEDGEMENTS

First, I would like to acknowledge my advisor, Dr. Steven L. Suib, whose encouragement, guidance, support and trust were essential to accomplish my Ph.D degree at UConn. His research enthusiasm, diversity, philosophy, and academic discipline have significantly affected me throughout my graduate study. I am also extremely grateful to Dr. Francis Galasso and Mrs. Lois Galasso, for their hospitality, generous help and encouragement on my research and graduate life in U.S. Many thanks as well to my committee: Drs. Prabhakar Singh, Alfredo Angeles-Boza, and Ray Joesten for their effort and help on my research.

I would also like to thank my teaching advisors: Drs. Fatma Selampinar and Edward Neth, whose enthusiastic attitude and philosophy toward teaching have really inspired me and also have strengthened my belief in future career as a teacher. I also want to thank the other UConn faculty and staff members: Dr. Lichun Zhang, Dr. Abhay Vaze, Dr. James Rusling, Emilie Hogrebe, Charlene Fuller, Osker Dahabsu, Ashely Butler, Adam Pangilinan, Brain Cardinal, and Daniel Daleb for their tireless support.

Special thanks to our former and current group members: Lei, Linping, Saminda, Guohong, Treese, Hui, Cecil, Fabian, Naftali, Anais, Aparna, Zhu, Chung-Hao, Yongtao, Altug, Curt, Nashaat, Gavin, Madhavi, Lakshitha, Sheng-Yu, Justin, Becca, Homer, Ting, Wenqiao, Jing, Mia, Wei, Junkai, Tehereh, and El-Sawy, who have shared valuable research experiences, provided lots of help and have also been so friendly to me during my graduate life.

Finally, my deepest gratitude goes to my family, my parents, my grandpa, who have cheered me on all the way through, especially my husband, Le, for his love and help during my graduate life. I could not have done this without their support.

TABLE OF CONTECTS

PART 1

Synthesis of Layered Ln₂O₂CO₃ (Ln: La, Nd, Sm, Eu) materials and Their Application as New series efficient and stable heterogeneous catalysts for biodiesel production

CHAPTER 1. INTRODUCTION	2
1.1.Overview	2
1.2.Significance and Background	3
1.2.1. Energy Crisis and Biodiesel	3
1.2.2. Comparisons of Biodiesel and Petro-diesel	3
1.2.3. Current Catalysts for Biodiesel Production	4
1.2.4. Layered Rare Earth Materials	5
CHAPTER 2. SYNTHESIS AND CHARACTERIZATION	6
2.1. Catalysts Synthesis	6
2.2. Characterization Methods	7
2.2.1. Thermogravimetric Analyses (TGA)	7
2.2.2. The Powder X-ray Diffraction (XRD)	7
2.2.3. Scanning Electron Microscope (SEM)	7
2.2.4. Transmission Electron Microscopy (HRTEM)	8
2.2.5. Brunauer Emmett Teller (BET)	8
2.2.6. Temperature Programmed Desorption (TPD-CO ₂)	8

2.2.7. Basic Strengths Tests by Indicators	9
2.2.8. Atomic Absorption Spectrometer (AAS)	9
2.2.9. Van Der Pauw Conductivity Tests	10
2.3. Catalytic Reactions and Products Analysis	12
2.3.1. Biodiesel Reactions	12
2.3.2. Biodiesel Yield Tests by Gas Chromatograph	12
CHAPTER 3. RESULTS	13
3.1. Characterization Results	13
3.1.1. Thermogravimetric analyses (TGA)	13
3.1.2. The Powder X-ray Diffraction (XRD)	15
3.1.3. Scanning Electron Microscope (SEM)	17
3.1.4. Transmission Electron Microscopy (HRTEM)	17
3.1.5. Brunauer Emmett Teller (BET)	20
3.1.6. Basic Strengths Tests by Indicators and TPD-CO ₂	20
3.2. Catalytic Reactions Results	21
3.2.1. Catalytic Results of Ln ₂ O ₂ CO ₃ Layered Materials at Different Temperatures	21
3.2.2. Catalytic Results of Different Amount of Catalysts used in biodiesel reactions	21
CHAPTER 4. DISCUSSION	25
4.1. Comparison of the Catalytic Activity of the Prepared Layered Nd ₂ O ₂ CO ₃ Material with Industrially Used Catalyst KOH	25

4.2. Comparison of the Catalytic Activity of the Potassium Contained Base and Ammonium Contained Base Synthesized Materials	28
4.3. Recyclability and Stability Tests of $\text{Ln}_2\text{O}_2\text{CO}_3$ Layered Materials	33
4.4. Leaching Tests	38
4.4.1. Potassium Amount Test by Flame Atomic Absorption Spectrometer (FAAS)	38
4.4.2 Potassium and Rare Earth Amount in Biodiesel Tests by X-ray Fluorescence (XRF)	40
4.5. Proposed Mechanism	41
CHAPTER 5. CONCLUSIONS	43

PART 2

The study of biodiesel production by using $\text{ZnO}/\text{Ln}_2\text{O}_2\text{CO}_3$ (Ln: La, Nd) as heterogeneous catalysts

CHAPTER 1. INTRODUCTION	45
1.1. Overview	45
1.2. Significance and Background	45
CHAPTER 2. SYNTHESIS AND CHARACTERIZATION	48
2.1. Catalysts Synthesis	48
2.2. Characterization Methods	48
2.2.1. Powder X-ray Diffraction (XRD)	48
2.2.2. Scanning Electron Microscope (SEM)	49

2.2.3. Transmission Electron Microscopy (HRTEM)	49
2.2.4. Thermogravimetric Analyses (TGA)	49
2.2.5. Temperature Programmed Desorption (TPD-CO ₂)	50
2.2.6. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)	50
2.3. Catalytic Reactions and Products Analysis	50
2.3.1. Biodiesel Reactions	50
2.3.2. Biodiesel Yield Tests by Gas Chromatograph	51
CHAPTER 3. RESULTS	52
3.1. Characterization Results	52
3.1.1. Powder X-ray Diffraction (XRD)	52
3.1.2. Scanning Electron Microscope (SEM)	57
3.1.3. Transmission Electron Microscopy (HRTEM)	57
3.1.4. Thermogravimetric Analyses (TGA)	59
3.1.5. Temperature Programmed Desorption (TPD-CO ₂)	60
3.2. Catalytic Reactions Results	61
3.2.1. The Effect of ZnO Amount in ZnO/La ₂ O ₂ CO ₃ in the Biodiesel Catalytic Reactions	61
3.2.2. The Effect of ZnO Amount in ZnO/Nd ₂ O ₂ CO ₃ in the Biodiesel Catalytic Reactions	62
3.2.3. Effect of Potassium Amount of Catalysts in Transesterification Reactions	63
CHAPTER 4. DISCUSSION	64

4.1. Effect of the Reaction Temperature in Transesterification Reactions	64
4.2. Effect of the Reaction Time in Transesterification Reactions	66
4.3. Effect of Amount of Catalysts Used in Transesterification Reactions	67
4.4. Effect of Methanol to Oil Molar Ratio in Transesterification Reactions	68
4.5. Effect of Water in Transesterification Reactions	69
4.6. Recyclability Tests of ZnO/La ₂ O(CO ₃) ₂ (Zn:Ln=1:2) Catalysts	70
CHAPTER 5. CONCLUSIONS	72

PART 3

Ongoing Work

Preliminary Study of the Hybrids of Nickel - Cobalt and Nickel - Zinc Layered Hydroxide Materials and their Electrochemical Properties

CHAPTER 1. INTRODUCTION	74
1.1. Overview	74
1.2. Significance and Background	74
CHAPTER 2. SYNTHESIS AND CHARACTERIZATION	76
2.1. Materials and Reagents	76
2.2. Catalysts Synthesis	76
2.3. Characterization Methods	76
2.3.1. Powder X-ray Diffraction (XRD)	76

2.3.2. Scanning Electron Microscope (SEM)	77
2.3.3. Transmission Electron Microscopy (HRTEM)	77
2.3.4. Energy Dispersive X-ray analysis (EDX)	77
2.3.5. Electrocatalytic Activity	78
CHAPTER 3. PRELIMINARY RESULTS	79
3.1. Characterization Results	79
3.1.1. Powder X-ray Diffraction (XRD)	79
3.1.2. Scanning Electron Microscope (SEM)	82
3.1.3. Transmission Electron Microscopy (HRTEM)	82
3.1.4. Energy Dispersive X-ray Analysis (EDX)	86
3.2. Electrocatalytic Activity Tests Results	87
CHAPTER 4. CONCLUSIONS	90
REFERENCES	91
FUTURE WORK	96
LIST OF PUBLICATIONS	97

LIST OF FIGURES

- Figure 1-1.** Van Der Pauw conductivity test set up. 11
- Figure 1-2.** TGA of prepared $\text{Ln}_2\text{O}(\text{CO}_3)_2$ samples (before calcination). 14
- Figure 1-3.** XRD patterns of a, synthesized $\text{Ln}_2\text{O}(\text{CO}_3)_2$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}$) solid materials before calcination (JCPDS 28-0512) and b, synthesized layered rare earth oxycarbonates materials $\text{Ln}_2\text{O}_2\text{CO}_3$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}$) after calcination (JCPDS 37-0804). 16
- Figure 1-4.** SEM images of $\text{Ln}_2\text{O}(\text{CO}_3)_2$ (before calcination), Ln : (a) La, (b) Nd, (c) Sm, and (d) Eu, and $\text{Ln}_2\text{O}_2\text{CO}_3$ (after calcination), Ln : (e) La, (f) Nd, (g) Sm, and (h) Eu. 18
- Figure 1-5.** TEM images of $\text{Ln}_2\text{O}_2\text{CO}_3$, Ln : (a) (b) La, (c) (d) Nd, (e) (f) Sm, and (g) (h) Eu. 19
- Figure 1-6.** Results of biodiesel (FAME) yield as a function of reaction temperature by layered $\text{Ln}_2\text{O}_2\text{CO}_3$ materials (Ln : La, Nd, Sm, Eu) (Conventional heating method, 5 wt. % catalysts loaded, reaction time: 1 hour, MeOH: Oil =1 by weight). 22
- Figure 1-7. (a)** Results of biodiesel (FAME) yield as a function of different catalyst amounts (weight %) of layered $\text{Ln}_2\text{O}_2\text{CO}_3$ materials (Ln : La, Nd, Sm, Eu) (conventional heating method, reactions temperature: 95 °C, reactions time: 1 hour, MeOH: Oil =1 by weight). 23
- Figure 1-7. (b)** Results of biodiesel (FAME) yield as a function of different catalyst amounts (weight %) of layered $\text{Ln}_2\text{O}_2\text{CO}_3$ materials (Ln : La, Nd) (microwave heating method, reactions temperature: 95 °C, reactions time: 30 min, MeOH: Oil =1 by weight). 24
- Figure 1-8. (a)** Results of biodiesel (FAME) yield as a function of reactions time (conventional heating method, reactions temperature: 95 °C, 5wt. % catalysts, MeOH: Oil =1 by weight). 26

Figure 1-8. (b) Results of biodiesel (FAME) yield as a function of reactions time (microwave heating method, reactions temperature: 95 °C, 5wt. % catalysts, MeOH: Oil =1 by weight). 27

Figure 1-9. XRD patterns of synthesized layered $\text{Ln}_2\text{O}_2\text{CO}_3$ (Ln: La and Nd) materials by using NH_3 and $(\text{NH}_4)_2\text{CO}_3$ (labeled as $\text{NH}_3\text{-Ln}_2\text{O}_2\text{CO}_3$) and KOH and K_2CO_3 (labeled as $\text{K-Ln}_2\text{O}_2\text{CO}_3$) as basic starting materials. 30

Figure 1-10. TEM pictures of (a), (b) potassium contained base synthesized $\text{Nd}_2\text{O}_2\text{CO}_3$ material and (c), (d) ammonium contained base synthesized $\text{Nd}_2\text{O}_2\text{CO}_3$ material. 31

Figure 1-11. The recyclability tests of layered $\text{Ln}_2\text{O}_2\text{CO}_3$ materials (Ln: La, Nd, Sm, Eu) (Conventional heating method, reactions temperature: 95 °C, 5 wt.% catalysts loaded, reactions time: 1 hour, MeOH: Oil = 1 by weight). 34

Figure 1-12. XRD patterns of (a) synthesized $\text{Ln}_2\text{O}(\text{CO}_3)_2$ (Ln = La, Nd, Sm, Eu) solid materials after 4th cycle of biodiesel reactions, ▲ are the peaks from Ln_2O_3 (b) synthesized layered rare earth oxycarbonate materials $\text{Ln}_2\text{O}_2\text{CO}_3$ (Ln = La, Nd, Sm, Eu) before reactions. 35

Figure 1-13. SEM images of $\text{Ln}_2\text{O}_2\text{CO}$ before reactions (a) La, (b): Nd, (c) Sm, and (d) Eu and after reactions, (e) La, (f) Nd, (g) Sm, and (h) Eu. 37

Figure 2-1. 3-steps reaction mechanism of transesterification reaction. 47

Figure 2-2. (a) XRD patterns of ZnO/ $\text{La}_2\text{O}_2\text{CO}_3$ materials at different Zn:La ratios, ▲ : $\text{La}_2\text{O}_2\text{CO}_3$ ★ : ZnO; and ▼ : new Zn-La layered materials. 53

Figure 2-2. (b) XRD patterns of ZnO/ $\text{Nd}_2\text{O}_2\text{CO}_3$ materials at different Zn:Nd ratios, ▲ : $\text{Nd}_2\text{O}_2\text{CO}_3$; ★ : ZnO. 54

Figure 2-3. SEM images of ZnO/La₂O₂CO₃ at different ratios before calcination (Zn/La = a 1/5, b 1/2, c 2/1, d 5/1) and after calcination (e, 1/5, f 1/2, g 2/1, h 5/1). 55

Figure 2-4. SEM images of ZnO/Nd₂O₂CO₃ at different ratios before (Zn/Nd = a 1/5, b 1/1, c 5/1) and after calcination (Zn/Nd = a 1/5, b 1/1, c 5/1). 56

Figure 2-5. TEM images of ZnO/Ln₂O₂CO₃ materials (Zn:Ln=1:5) Ln: La (a) (b), Nd (c) (d).58

Figure 2-6. TGA of selected ZnO/La₂O(CO₃)₂ (Zn:Ln=1:2) before calcination. 59

Figure 2-7. TPD-CO₂ profile of selected ZnO/La₂O₂CO₃ (Zn:Ln=1:2). 60

Figure 2-8. FAME yields as a function of the Zn to La ratio. 61

Figure 2-9. FAME yields as a function of the Zn to Nd ratio. 62

Figure 2-10. FAME yields as a function of Zn to Nd ratio and the amount of potassium in the catalysts (conventional heating method; reaction temperature: 95 °C; reaction time: 1 hour; catalysts weight percentage: 5 %; MeOH: Oil =1 by weight). 63

Figure 2-11. FAME yields as a function of reaction temperature by ZnO/La₂O(CO₃)₂ (Zn:Ln=1:2) catalyst (conventional heating method; reaction time: 1 hour; catalysts weight percentage: 5 %; MeOH: Oil =1 by weight). 65

Figure 2-12. FAME yields as a function of time by ZnO/La₂O(CO₃)₂ (Zn:Ln=1:2) catalysts (conventional heating method; reaction temperature: 95 °C; catalysts weight percentage: 5 %; MeOH: Oil =1 by weight). 66

Figure 2-13. FAME yields as a function of catalysts weight percentage by ZnO/La₂O(CO₃)₂ (Zn:Ln=1:2) catalysts (conventional heating method; reaction temperature: 95 °C; reaction time: 1 hour; MeOH: Oil =1 by weight). 67

- Figure 2-14.** FAME yields as a function of methanol oil molar ratio by ZnO/La₂O(CO₃)₂ (Zn:Ln=1:2) catalysts (conventional heating method; reaction temperature: 95 °C; reaction time: 1 hour; catalysts weight percentage: 5 %). 68
- Figure 2-15.** FAME yields as a function of water percentage in the reaction system (conventional heating method; reaction temperature: 95 °C; reaction time: 1 hour; catalysts weight percentage: 5 %; MeOH: Oil =1 by weight). 69
- Figure 2-16.** FAME yields as a function of cycle number in the biodiesel reaction system (conventional heating method; reaction temperature: 95 °C; reaction time: 1 hour; catalysts weight percentage: 5 %; MeOH: Oil =1 by weight). 71
- Figure. 3-1.** X-ray diffraction patterns of Ni-Co hydroxides. 80
- Figure. 3-2.** X-ray diffraction patterns of Ni-Zn hydroxides. 81
- Figure. 3-3.** SEM images of Ni-Co hydroxides at different Ni:Co ratios. 83
- Figure. 3-4.** SEM images of Ni-Zn hydroxides at different Ni:Co ratios. 84
- Figure. 3-5.** HRTEM images of selected Ni-Co hydroxides at different Ni:Co ratios. 85
- Figure. 3-6.** Cyclic voltammetry of selected samples (a) comparison between Ni-Co hydroxides and pure nickel hydroxide; (b) comparison between Ni-Zn hydroxides and pure nickel hydroxide. 88
- Figure. 3-7.** The calculation of numbers of electron transferred for Ni:Co=9:1 hydroxide catalyst in the oxygen reduction reactions. 89

LIST OF TABLES

Table 1-1. BET surface area and basic strength tests by indicators and TPD-CO ₂ .	20
Table 1-2. Biodiesel yields of potassium and ammonium based Ln ₂ O ₂ CO ₃ materials.	32
Table 1-3. The potassium amount in fresh and recycled Ln ₂ O ₂ CO ₃ materials.	39
Table 1-4. The potassium and rare earth metal amount in biodiesel.	40
Table 3-1. Atomic percentage measurement of Ni-Co hydroxides by EDX.	86

LIST OF SCHEME

Scheme 1-1. Catalytic mechanism of Ln ₂ O ₂ CO ₃ layered materials in biodiesel reactions.	42
--	----