

CHARACTERIZATION OF CALCIUM OXIDE PREPARED BY HYDRATION-
DEHYDRATION METHOD

NURUHUDA BINTI WAHAB

UNIVERSITI TEKNOLOGI MALAYSIA

CHARACTERIZATION OF CALCIUM OXIDE PREPARED BY HYDRATION-
DEHYDRATION METHOD

NURUHUDA BINTI WAHAB

A dissertation submitted in partial fulfillment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

DECEMBER 2010

*To my beloved mother and father
Thank you for your support and courage*

ACKNOWLEDGEMENT

First and foremost, all praise be to Allah S. W. T for His blessings and guidance for giving me the inspiration to complete this project. Also, I would like to express my sincerest appreciation to my project supervisor, Prof. Dr. Abdul Rahim Yacob for giving me valuable advices, motivation and spending his precious time to guide and help me throughout this project.

Furthermore, I would also like to express my gratitude to all lab assistants for their help in every way they could. I also thanks to all my colleges and others who always give me support and sharing of knowledge. Their opinion and tips are very useful while preparing this thesis.

Last but not least, I wish to express my sincere appreciation to my beloved family for their continuous encouragement, advices and pray to give me the strength in completing my research.

ABSTRACT

Calcium oxide, CaO is an important inorganic catalyst, used in toxic waste remediation agent and adsorbent. In this study, CaO was prepared by hydration-dehydration method using commercial calcium oxide as starting material, converted into its hydroxide by sonicating it in ultrasonic water bath for one hour, then, undergone dehydration step by heating under high vacuum at different temperatures which were 200, 300, 400, 500, 600, 700 and 800°C respectively. The prepared samples were characterized using several techniques including Thermal Gravimetry Analysis (TGA), Fourier Transform Infrared (FT-IR), X-Ray Diffraction (XRD), Nitrogen Gas Adsorption (NA) and Field Emission Scanning Electron Microscope (FESEM). The FT-IR shows that the elimination of hydroxide and carbonate species increased with the increasing calcination temperature. By XRD, the prepared CaO-700 shows the smallest particle size which is 27.93 nm compared to commercial CaO with particle size of 37.14 nm. The basicity study of the prepared CaO carried out using back titration method showed that the prepared CaO-800 was found to be very high basic which is 1.78 mmol/g. The result obtained using Electron Spin Resonance spectroscopy to the CaO-800 irradiation by UV in H₂, showed that the cavity of CaO-800 was too large to trap electrons, containing several impurities such as manganese, Mn²⁺ that might inhibit the formation of trapped electron in CaO.

ABSTRAK

Kalsium oksida, CaO merupakan mangkin bukan organik yang penting, digunakan sebagai bahan perawat sisa toksik dan bahan penjerap. Dalam kajian ini, CaO disediakan melalui kaedah penghidratan-penyahhidratan menggunakan kalsium oksida komersial sebagai bahan pemula yang kemudian ditukarkan kepada kalsium hidroksida melalui aliran gelombang bunyi di dalam rendaman air selama satu jam. Seterusnya, proses penyahhidratan kalsium hidroksida yang terhasil dijalankan melalui pemanasan pada pelbagai suhu iaitu 200, 300, 400, 500, 600, 700 dan 800°C menggunakan vakuum berkuasa tinggi. Pencirian sampel dilakukan menggunakan kaedah pencirian Pemetran Gravitasi Haba, Spektroskopi Inframerah, Pembelauan Sinar-X, penjerapan nitrogen dan Mikroskop Imbasan Elektron. Spektroskopi inframerah menunjukkan penyingkiran molekul hidroksida dan karbonat meningkat dengan peningkatan suhu pemanasan. Analisis menggunakan pembelauan sinar-X menunjukkan sampel CaO-700 menghasilkan saiz partikel paling kecil, iaitu 27.93 nm berbanding CaO komersial dengan saiz partikel 37.14 nm. Keputusan ujian bes melalui kaedah pentitratan semula menunjukkan sampel CaO-800 paling berbes iaitu 1.78 mmol/g. Keputusan dari Resonans Spin Elektron ke atas sampel CaO-800 yang dikenakan sinaran UV dan dialirkan dengan gas hidrogen menunjukkan rongga yang terbentuk adalah terlalu besar untuk memerangkap elektron. Tambahan pula terdapat bendasing mangan, Mn, yang menghalang pemerangkapan elektron pada CaO.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF SCHEMES	xiii
	LIST OF ABBREVIATIONS	xiv
	LIST OF APPENDIX	xv
1	INTRODUCTION	1
	1.1 Background of Research	1
	1.2 Statement of Problem	3
	1.3 Objectives of Study	3
	1.4 Scope of Study	4
	1.5 Significance of Study	4
2	LITERATURE REVIEW	5
	2.1 Calcium Oxide	5
	2.2 Surface Defects	7
	2.3 Ultrasonic Energy	9

2.4	Solid acid and base catalyst	10
2.5	Application of Characterization Technique to CaO	13
2.5.1	Fourier Transform Infrared	13
2.5.2	Thermogravimetric Analysis	15
2.5.3	Field Emission Scanning Electron Microscopy (FESEM)	17
2.5.4	Nitrogen Gas Adsorption	18
2.5.4.1	Determination of surface area by Single Point Brunauer, Emmet and Teller (BET) Method	19
2.5.5	X-ray Powder Diffraction (XRD)	21
2.5.6	Electron Spin Resonance (ESR)	24
3	RESEARCH METHODOLOGY	29
3.1	Chemical Reagents	29
3.2	Sample Preparation	30
3.2.1	Preparation of Calcium Hydroxide by Hydration Method	30
3.2.2	Preparation and Activation of High Surface Area CaO by Dehydration Method	30
3.3	Instrumentations	33
3.4	Characterization of Basicity Strength	34
3.4.1	Back-Titration	34
3.4.2	Electron Spin Resonance (ESR)	36
4	RESULTS AND DISSCUSSION	38
4.1	Introduction	38
4.2	Characterizations	38
4.2.1	Thermal Gravimetry Analysis	38
4.2.2	Fourier Transform Infrared	41
4.2.3	X-ray Powder Diffraction Analysis	46

4.2.3.1	Crystallite Size	53
4.2.4	Surface Study Using Nitrogen Gas Adsorption	54
4.2.5	Field Emission Scanning Electron Microscope	55
4.2.6	Basicity Study	60
4.2.7	Electron Spin Resonance Study	62
5	CONCLUSION	65
	REFERENCES	67
	APPENDIX	76

LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Physical properties of CaO	6
2.2	Acid-base theories	11
3.1	Chemical reagents and its molecular formula	29
4.1	Percentage of weight loss at different temperature regions	39
4.2	Peak assignment for commercial CaO	42
4.3	Peak assignment for Ca(OH) ₂	43
4.4	Peak assignment for all prepared CaO.	45
4.5	XRD peak assignment for commercial CaO and Ca(OH) ₂	46
4.6	XRD peaks assignment for prepared CaO	48
4.7	Average particle size for commercial CaO, prepared Ca(OH) ₂ and all prepared CaO with different calcination temperatures	53
4.8	Specific BET surface area for CaO, Ca(OH) ₂ and prepared nano CaO	54
4.9	Amount of basicity for commercial CaO, prepared Ca(OH) ₂ and all prepared CaO	61

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Schematic representation of the trapped electron centers on the surface of MgO	9
2.2	Schematic illustration of (a) isolated hydroxyl and (b) adsorbed water molecules	14
2.3	Schematic illustration of (a) monodentate carbonate (b) bidentate carbonate	14
2.4	Bragg's Law	23
2.5	The schematic diagram of an ESR spectrometer	26
2.6	Zeeman energy levels of an electron in an applied magnetic field	27
3.1	Schematic diagram of vacuum pump system	31
3.2	Flow chart for preparing high surface area CaO by hydration-dehydration method	32
3.3	ESR sample cell	36
4.1	TGA of Ca(OH) ₂	39
4.2	Percentage of weight loss at different temperature regions from TGA	40
4.3	FT-IR spectrum for commercial CaO	42
4.4	FT-IR spectrum for Ca(OH) ₂	43
4.5	FTIR spectra of prepared CaO-200, CaO-300, CaO-400, CaO-500, CaO-600 CaO-700 and CaO-800	44
4.6	XRD diffractogram for commercial CaO and prepared Ca(OH) ₂	47
4.7	XRD diffractogram for (a) Ca(OH) ₂ , (b) CaO-200, (c) CaO-300, (c) CaO-400, (d) CaO-500, (e) CaO-600, (f) CaO-700, (g) CaO-800	51

4.8	BET Surface Area for CaO, Ca(OH) ₂ and prepared CaO	55
4.9	(a) FESEM micrograph for commercial CaO with magnification 5 kX	56
	(b) FESEM micrograph for commercial CaO with magnification 10 kX	57
4.10	(a) FESEM micrograph for commercial Ca(OH) ₂ with magnification 5 kX	58
	(b) FESEM micrograph for commercial Ca(OH) ₂ with magnification 10 kX	58
4.11	(a) FESEM micrograph for prepared CaO-700 with magnification 5 kX	59
	(b) FESEM micrograph for prepared CaO-700 with magnification 10 kX	60
4.12	Basicity of prepared CaO compared to commercial CaO and Ca(OH) ₂	62
4.13	ESR spectra obtained for CaO-800 exposed with hydrogen after 20 minutes irradiation with UV	63

LIST OF SCHEME

SCHEME NO.	TITLE	PAGE
3.1	Mechanism in determination the amount of basic sites for nano CaO	35

LIST OF ABBREVIATIONS

CaO	-	Calcium oxide
Ca(OH) ₂	-	Calcium hydroxide
ESR		Electron Spin Resonance
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared
HCl	-	Hydrochloric acid
H ₂	-	Hydrogen
ICSD	-	Inorganic Crystal Structure Database
KBr	-	Potassium bromide
Mn	-	Manganese
NaOH	-	Sodium hydroxide
nm	-	Nanometer
TGA	-	Thermogravimetric analysis
UV	-	Ultra violet
XRD	-	X-Ray Powder Diffraction

LIST OF APPENDIX

APPENDIX NO.	TITLE	PAGE
A	Sample calculation for particle size, D using Schererr's Equation	76

CHAPTER 1

INTRODUCTION

1.1 Background of the research

Recently, metal oxides have undergone rapid technological and commercial interest due to their important role in corrosion protection, catalysis, sensors, fuel cells and ceramics. In the catalysis industry, alkaline earth metal oxide is one of the most well-researched catalysts. Alkaline earth metal oxide such as MgO, CaO and BaO have displayed a highly active catalysis for certain base-catalyzed reaction such hydrogenation, nitroaldol reaction and transesterification (Koper, *et al.*, 1997).

Base-catalyzed reaction can be identified as chemical reaction that occurs when the reactants act as acid toward catalyst that act as a base. Certain metal oxides with a single component were found to act as solid base catalysts in the absence of such alkali metals as Na and K. The material may be called solid base catalyst only if it acts as a base toward the reaction by donating an electron pair (Lewis base) or abstraction of proton (Bronsted base) to form anionic intermediates that will undergo catalytic cycles. Alkaline earth metal oxides have shown their potentials as base catalyst due to its properties which can abstract H^+ from reactants or hydrogen gas or can donate electron pair for starting the reactions (Hattori, 2001).

On the other hand, alkaline earth metal oxides possess highly reactive sites. Highly reactive sites will form the basic site or acidic site of the catalyst (Hattori, 2001). Generally, the reactive sites of the metal oxides depend on their surface

defects. The preparation method and activation procedures will be the factors in determining surface concentration and reactivity of such sites. Besides that, the pathway of electron to move from oxide surface to the adsorbed molecules is also important in order to determine the reactive sites. The pathway of consequence reaction strongly depends on the particular surface sites available, also on the nature of the adsorbing molecule.

Physical and chemical characteristics of the prepared metal oxides depend on their preparation methods. Alkaline earth metal oxides are generally prepared by thermal decomposition of alkaline earth metal compounds such as hydroxides, chlorides, sulfates and carbonates. Thermal decomposition of hydroxides and carbonates in air or under vacuum is the most general methodology used to prepare alkaline earth metal oxides as basic catalyst. Decomposition of hydroxide is frequently used to prepare MgO and CaO, whereas BaO and SrO are prepared from the corresponding carbonates as precursor salt (Corma and Iborra, 2006).

The study in catalysis is also related to nanotechnology. Catalysis has been the traditional field of surface chemistry. Due to the initiation of nanotechnology, the control of material on molecular scale at surface becomes more important. The nanosize scale approximately 1 to 100 nm is important in developing nanostructured catalyst. Nano-scale particles with high surface area yield a number of defect sites. The most common defects are coordinatively unsaturated ions arising from edge, corners, anion/cation vacancies and electron excess center (Kolansiski, 2008). Besides that, confinement effects can completely alter the chemical characteristics of sufficiently small nanoparticles. Researchers have also shown that the atomic characteristics of metallic nanoparticles, including particle size and surface composition, are critical to catalytic activity and selectivity.

In this research, hydration-dehydration method assisted with ultrasonic treatment was used in order to create nano-CaO with high surface area and high basicity thus increased its catalytic performance. Hydration-dehydration method was conducted to prepare CaO at various temperatures under vacuum atmosphere. The

correlation between basicity and temperature calcinations during preparation was studied.

1.2 Statement of Problem

In industry, transesterification of palm oil to biodiesel utilizes homogeneous base catalysts such sodium and potassium hydroxide (NAOH and KOH) dissolve in methanol which is a corrosive liquid. However, this process is time consuming and involves expensive separation step. This process is also a non-environmental friendly because implies the consumption of large amount of water for wet washing to remove the salt produced from neutralization process and the residual acid or base catalyst.

The utilization of a successful heterogeneous solid base catalyst will manage most of the economical and environmental drawbacks of a homogeneous process. Heterogeneous catalysts are non-corrosive and environmental friendly. They are also much easier to be separated from liquid products, and can be designed to give higher activity, more selectivity and longer catalyst lifetime. This study used calcium oxide, CaO which is a base catalyst from alkaline earth metal oxide to prepare materials with high surface areas and higher basicity to improve the catalytic properties of these materials thus overcome the drawbacks of homogeneous catalysts in industry.

1.3 Objective of Study

The objectives of this research were to investigate the characteristics and also to study the basicity of prepared CaO. This research's aims are divided into three:

- 1) To prepare CaO from commercial CaO by sonicating and thermal decomposition at various temperatures by using vacuum and pump system.

- 2) To characterize and study the basicity of all prepared CaO.
- 3) To compare the characteristics between commercial, hydrated and the prepared CaO.

1.4 Scope of Study

The scope of the research was to prepare and characterize physico-chemical properties of prepared CaO. This study used commercial CaO as precursor that was sonicated by using ultrasonic water and was undergone thermal decomposition/activation known as dehydration method at various temperatures, 200°C to 800°C using vacuum line system.

The characterization of prepared CaO was done using Thermogravimetry Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Single Point Surface Area- nitrogen adsorption and Field Emission Scanning Electron Microscopy (FESEM). The basicity test was also conducted via back titration method and further strengthens by using ESR.

1.5 Significance of Study

As we know, metal oxide is widely used as catalyst especially in biodiesel production. This study was carried out one of metal oxides that also used as catalyst which is calcium oxide. Commercial calcium oxide was synthesized to produce high surface area and high basicity of calcium oxide that can be used and applied in catalysis industry.

REFERENCES

- Abdel Halim, W. S. and Shalabi, A. S. (2004). Surface morphology and interaction between water and MgO, CaO and SrO surfaces Periodic HF and DFT calculations. *Appl. Surf. Sci.* 221: 53–61.
- Abdul Rahim Yacob (1998). *An ESR Study of Alkali Metals Trapped in Cryogenic Matrices and on Metal Oxides Surfaces*. Ph.D. Thesis. University of Wales, Cardiff.
- Alavi, M. A. and Morsali, A. (2010). Ultrasonic-assisted synthesis of Ca(OH)₂ and CaO nanostructures. *J. Exp. Nanosci.* 5(2): 93-105.
- Albuquerque, M. C. G., Azevedo, D. C. S., Cavalcante, C. L., Gonzales, J. S., Robles, J. M. M., Tost, R. M., Castellon, E. R., Lopez, A. M. and Torres, P. M. (2009). Transesterification of ethyl butyrate with methanol using MgO / CaO catalyst. *J. Mol. Catal. A: Chem.* 300: 19-24.
- Aramendia, M. A., Benitez, J. A., Jimenez, V. B. C., Marinas, J. M., Ruiz, J. R. and Urbano, F. (1999). Characterization of Various Magnesium Oxides by XRD and ¹H MAS NMR Spectroscopy. *J. Solid State Chem.* 144: 25-29.
- Atkins, P. and Paula, J. D. (2002). *Physical Chemistry*. (7th ed.). New York: Oxford University Press.
- Bellobono, I. R., Castellano, L. and Tozzi, A. (1991). Sulphur Dioxide Control by Reactive Photografted Membranes Innobilizing High Surface Area Calcium Oxide. *Mater. Chem. Phys.* 28: 69-75.

- Bernal, S., Calvino, J. J., Cauqui, M. A., Izquierdo, J. M. R. and Vidal, H. (1995). Synthesis, characterization and performance of sol-gel prepared $\text{TiO}_2\text{-SiO}_2$ catalysts and supports. *Stud. Surf. Sci. Catal.* 91: 461-471.
- Beruto, D., Barco, L., Seary, A. and Spinol, G. (1980). Characterization of the porous CaO particles formed by decomposition of CaCO_3 and Ca(OH)_2 in vacuum. *Am. Ceram. Soc. Bull.* 63: 439-443.
- Bianchi, C. L., Carli, R., Fontaneto, C. and Ragaini, V. (1995). Preparation of highly dispersed supported catalysts by ultrasound. *Stud. Surf. Sci. Catal.* 91: 1095-1100.
- Boey, P. L., Maniam, G. P. and Hamid, S. A. (2010). Biodiesel production via transesterification of palm oil using waste mud crab (*Scylla serrata*) as a heterogeneous catalyst. *Bioresour. Technol.* 100: 6362-6368.
- Bosch, P., Lopez, T., Asomoza, M., Gomez, R., Cauqui, M. A. and Izquierdo, J. M.R. (1995). Pt/SiO₂ Sonogels: Synthesis and Characterization. *Langmuir.* 11: 4328-4332.
- Boudart, M., Delbouille, A., Derouane, E. G., Indovina, V. and Walters, A. B. (1972). Activation of hydrogen at 78.deg.K on paramagnetic centers of magnesium oxide. *J. Am. Chem. Soc.* 94: 6622-6630.
- Brown, M. E. (1988). *Introduction to Thermal Analysis, Techniques and Applications*. London: Chapman and Hall.
- Charsley, E. L. and Warrington, S. B. (1992). *Thermal Analysis-Techniques and Applications*. London: Royal Society of Chemistry.
- Chiesa, M., Paganini, M. C. and Giamello, E. (1997). Surface Color Centers on Calcium Oxide: An Electron Paramagnetic Resonance Investigation. *Langmuir.* 13(20): 5306-5315.

- Cho, Y. B., Seo, G. and Chang, D. R. (2009). Transesterification of Tributyrin With Methanol over CaO from Various Precursors. *Fuel Process. Technol.* 90: 1252-1258.
- Colthup, N. B., Daily, L. H. and Wiberly, S. E. (1964). *Introduction to IR and Raman Spectroscopy*. New York: Academic Press.
- Corma, A. and Iborra, S. (2006). Optimization of Alkaline Earth Metal Oxide and Hydroxide Catalyst for Base Catalyst Reactions. *Adv. Catal.* 49: 239-302.
- Cullity, B. D. (1978). *Element of X-ray Diffraction*. London: Addison Wesley.
- Dhas, N. A., Koltypin, Y. and Gedanken, A. (1997). Sonochemical Preparation and Characterization of Ultrafine Chromium Oxide and Manganese Oxide Powders. *Chem. Mater.* 9(12): 3159-3163.
- Egerton, R. F. (2005). *Physical principle of electron microscopy*. U. S. A: Springer Science.
- Flohr, J. K. (1997). *X-ray Powder Diffraction*. London: Elsevier.
- Garcia, J., Lopez, T., Alvarez, M., Aguilar, D. H. and Quintana, P. Spectroscopic, structural and textural properties of CaO and CaO-SiO₂ materials synthesized by sol-gel with different acid catalysts. *J. Non-Cryst. Solids.* 354: 729-732.
- Giamello, E., Paganini, M. C., Chiesa, M. and Martino, P. (2002). EPR Study of the Surface Basicity of Calcium Oxide: The CaO-NO Chemistry. *J. Phys. Chem. B.* 106(48): 12 531-12 536.
- Granados, M. L., Poves, M. D. Z., Alonso, D. M., Mariscal, R., Galisteo, F. C., Moreno, T. R., Santamaria, J. and Fierro, J. L. G. (2007). Biodiesel from sunflower oil by using activated calcium oxide. *Appl. Catal., B.* 73: 317-326.

- Griffiths, P. R. and Haseth, J. A. D. (1986). *Fourier Transform Infrared Spectrometry*. New York: J. Wiley.
- Hattori, H. (2001). Solid Base Catalysts: Generation of Basic Sites and Application to Organic Synthesis. *Appl. Catal., A*. 222: 247-259.
- Heal, G. R. and Haines, P. J. (2002). *Principals of thermal analysis and calorimetry*. United Kingdom: Royal Society of Chemistry.
- Henderson, B. and Tomlinson, A. C. (1969). Some studies of Defects in Calcium Oxide-II. Intrinsic Lattice Defects. *J. Phys. Chem. Solids*. 30: 1801-1809.
- Henderson, B. and Wertz, J. E. (1977). *Defects in Alkaline Earth Oxides*. New York: Halsted Press.
- Huaping, Z., Zongbin, W., Yuanxiong, C., Ping, Z., Shijie, D., Xiaohua, L. and Zongqiang, M. (2006). *Chinese J. Catal.* 27(5): 391-396.
- Hussain, A. and Mohd Saiyudi, N.K.W. (2005). *Introduction to Surface and Colloid Chemistry Monograph*. Johor: Universiti Teknologi Malaysia.
- Igor, N. M. and Abdelhamid, S. (2008). Comparative Study of Triglyceride Transesterification in the Presence of Catalytic Amounts of Sodium, Magnesium and Calcium. *Appl. Catal., A*. 399: 45-52.
- Ito, T., Wang, J. X., Lin, C. H. and Lunsford, J. H. (1985). Oxidative dimerization of methane over a lithium-promoted magnesium oxide catalyst. *J. Am. Chem. Soc.* 107: 5062–5068.
- Kawashima, A., Matsubara, K. and Honda, K. (2009). Acceleration of catalytic activity of calcium oxide for biodiesel production. *Bioresour. Technol.* 100: 696–700.

- Keatch, C. J. and Dollimore, D. (1975). *An Introduction into Thermogravimetry*. (2nd. ed.). London: Heyden and Sons.
- Knozinger, E., Diwald, O. and Sterrer, M. (2000). Chemical Vapour Deposition-A New Approach to Reactive Surface Defects of Uniform Geometry on High Surface Area Magnesium Oxide. *J. Mol. Catal. A: Chem.* 162: 83- 95.
- Koper, O. B., Lagadic, I., Volodin, A. and Klanbude, K. J. (1997). Alkaline-Earth Metal Oxide Nanoparticles Obtained by Aerogel Methods. Characterization and Rational for Unexpectedly High Surface Chemical Reactivities. *Chem. Mater.* 9: 2468-2480.
- Kolansiski, K. W. (2008). *Foundation of Catalysis and Nanostructure*. England: J. Wiley.
- Kouzu, M., Kasuno, T., Tajika, M., Yamanaka, S. and Hidaka, J. (2008). Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. *Applied Catal., A.* 334: 357–365.
- Kulkarni, D. and Wachs, I. E. (2002). Isopropanol oxidation by pure metal oxide catalysts: Number of active surface sites and turnover frequencies. *Appl. Catal., A.* 237: 121-137.
- Kumar, D. and Ali, A. (2010). Nanocrystalline Lithium Ion Impregnated Calcium Oxide As Heterogeneous Catalyst for Transesterification of High Moisture Containing Cotton Seed Oil. *Energy Fuels.* 24: 2091–2097.
- Kunz, U., Binder, C. and Hoffmann, U. (1995). Preparation of fine particles as catalysts and catalyst precursors by the use of ultrasound during precipitation. *Stud. Surf. Sci. Catal.* 91: 869-878.
- Leeuw, D. N. H. and Burton, J. A. (2001). Density-functional theory calculations of the interaction of protons and water with low-coordinated surface sites of calcium oxide. *Phys. Rev. B: Condens. Matter.* 63: 195-204.

- Lindley, J. (1992). Sonochemical effects on syntheses involving solid and supported catalysts. *Ultrasonics*. 30: 163-167.
- Maniatis, Y. and Mandi, V. (1992). Electron Paramagnetic Resonance signals and effects in marble induced in working. *J. Appl. Phys.* 71. 4859-4867.
- Mertinez, J. G., Lopez., A. B., Gania, A. G. and Solano, A. L. (2002). SO₂ Retention at Low Temperature by Ca(OH)₂-Derived CaO: A Model for CaO Regeneration. *Fuel*. 81: 305-331.
- Motabadi, H., Salamatinia, B., Bhatia, S. and Abdullah, A. Z. (2010). Ultrasonic Assisted Biodiesel Production Process From Palm Oil Using Alkaline Earth Metal oxides As The Heterogeneous Catalysts. *Fuel*. 89: 1818-1825.
- Murphy, D. M., Farley, R. D., Purnell, I. J., Rowlands, C. C. and Yacob, A. R. (1999). Surface Defect Sites Formed on Partially and Fully Dehydrated MgO: An EPR/ENDOR Study. *J. Phys. Chem. B*. 103: 1944-1953.
- Nakatani, N., Takamori, H., Takeda, K. and Sakugawa, H. (2009). Transesterification of soybean oil using combusted oyster shell waste as a catalyst. *Bioresour. Technol.* 100: 1510–1513.
- Neppolian, B. Q., Jung, W. H. and Choi, H. (2008). Ultrasonic-assisted sol-gel method of preparation of TiO₂ nano-particles: Characterization, properties and 4-chlorophenol removal application. *Ultrason. Sonochem.* 15: 649-658.
- Nieves, I. and Klabunde, K. J. (1988). Nature of Chemisorbed Species On Metal Oxide Surfaces, Electron Transfer and Bond Breaking Process. *Mater. Chem. Phys.* 18: 485-498.
- Olga, B. K., Isabelle, L. and Alexander, V. (1997). Alkaline-Earth Oxide Nanoparticles Obtained by Aerogel Methods, Characterization and Rational for Unexpected Highly Surface Chemical Reactivities. *Chem. Mater.* 9: 2468-2480.

- Oatley, C.W. (1972). *The Scanning Electron Microscopy*. Cambridge: Cambridge University Press.
- Ozawa, T. (2000). Thermal Analysis-Review and Prospect. *Thermochim. Acta*. 355: 35-42.
- Perego, G. (1998). Characterization of heterogenous catalyst by X-ray Diffraction techniques. *Catal. Today*. 41: 251-259.
- Peterson, G. R. and Scarrah, W. P. (1984). Rapeseed oil transesterification by heterogeneous catalysis. *J. Am. Oil Chem. Soc.* 61. 1593–1597.
- Potgieter, S. S., Strydom, C. A and Gheevarghese, O. (2003). The effect of ultrasonic energy on lime slaking. *Miner. Eng.* 16: 767-77.
- Samadi, N. S., Amat Mustajab, M. K. and Yacob, A.R. (2010). Activation Temperature Effect on the Basic Strength of Prepared Aerogel MgO. *Int. J. Basic Appl. Sci.* 10. 20-23.
- Seletchi, E. D. (2007). Principles and Methods of Electron Paramagnetic Resonance: Dating and Dosimetry. *J. Phys.* 52: 393-400
- Suslick, K. S., Choe, S. K., Cichowlas, A. A. and Grinstaff, M. W. (1991). Sonochemical synthesis of amorphous iron. *Nature*. 353: 414 – 416.
- Symons, M. (1978). *Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy*. New York: J. Wiley.
- Tai, A., Kikukawa, T., Sugimura, T., Inoue, Y., Abe, S., Osawa, T. and Harada, T. (1993). Highly Efficient Enantio-Differentiating Hydrogenation Catalyst Prepared from Ultrasonicated Raney Nickel by Asymmetric Modification. *Stud. Surf. Sci. Catal.* 75: 2443-2446

- Tanabe, K. and Holderich, W. F. (1999). Industrial Application of Solid Acid-Base Catalyst. *Appl. Catal., A*. 181: 399-434.
- Tanabe, K., Misono, M., Ono, Y. and Hattori, H. (1989). *New Solid Acids and bases: Their Catalytic Properties*. Tokyo: Kadansha-Elsevier.
- Tang, Z. X., Claveau, D., Corcuff, R., Belkacemi, K. and Arul, J. (2008). Preparation of nano-CaO using thermal-decomposition method. *Mater. Lett.* 62: 2096–2098.
- Tanimoto, D. H. and Kemp, J. C. (1966). Forbidden Hyperfine Transitions in the Electron Spin Resonance of Mn^{2+} in CaO and SrO crystals. *J. Phys. Chem. Solids*. 27: 887-891.
- Wei, Z., Xu, C. and Li, B. (2009). Application of waste eggshell as low-cost solid catalyst for biodiesel production. *Bioresour Technol.* 100: 2883–2885.
- Wertz, J. E. and Bolton, J. R. (1973). *Electron Spin Resonance: Elementary Theory and Practical Applications*. United State of America: McGraw Hill.
- Xi, Y. and Davis, R. J. (2008). Influence of water on the activity and stability of activated Mg-Al hydrotalcites for the transesterification of tributyrin with methanol. *J. Catal.* 254: 190-197.
- Xuejun, L., Huayang, H., Shenlin, Z. and Xianglan, P. (2008). Transesterification of Soybean Oil to Biodiesel Using CaO as a Solid Base Catalyst. *Fuel*. 87: 216-221.
- Yoosuk, B., Udomsap, P., Puttasawat, B. and Krasae. P. (2010). Modification of calcite by hydration-dehydration method for heterogeneous biodiesel production process: The effects of water on properties and activity. *Chem. Engin. J.* 162: 135-141.

Zabeti, M., Wan Daud, W. M. A. and Aroua, M. K. (2010). Biodiesel production using alumina-supported calcium oxide: An optimization study. *Fuel Process. Technology*. 91: 243–248.