MODIFIED ZEOLITE BETA AS CATALYSTS IN FRIEDEL-CRAFTS ALKYLATION OF RESORCINOL

MARZITA BT ABD MAZAK

UNIVERSITI TEKNOLOGI MALAYSIA

MODIFIED ZEOLITE BETA AS CATALYSTS IN FRIEDEL-CRAFTS ALKYLATION OF RESORCINOL

MARZITA ABD MAZAK

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

FEBRUARY 2006

Special dedicated for:

my beloved mother and father, my parents in law

my husband, Muhazar Mohammad and my beloved daughter,

Fatin Afrina

ACKNOWLEDGEMENT

Alhamdulillah, all praise be to Allah. The supreme Lord of the world. Peace and blessing to Nabi Muhammad S. A. W, all the Prophets, his families and all muslims.

First of all, I would like to thank my project supervisor, Assoc. Prof. Dr. Zainab Ramli for her patience in supervising, critics and giving thoughtful guidance with knowledge towards the completion of this research. Her encouragement, understanding and supervision are very much appreciated. I am also very thankful to my co-supervisor, Assoc. Prof. Dr. Farediah Ahmad for her guidance, advices and motivation. Without their continued support and interest, this thesis would not have been the same as presented here.

I would like to thank MOSTI, IRPA under vote no: 74507 and PTP, UTM for scholarship and financial support. I also would like to express my sincere appreciation to all lecturers and researchers in the Zeolite and Porous Material Group (ZPMG) of UTM, Department of Chemistry, and Ibnu Sina Institute, in particular Prof. Dr. Halimatun Hamdan, Assoc. Prof Dr. Salasiah Endud, Dr Hadi Nur, Assoc. Prof. Dr. Rahim Yaakob, Mr Didik Prasetyoko, Mr Lim Kheng Wei and others, who have also giving me advices and valuable suggestions for conducting this research.

Thanks to all the lab assistants, Mr Kadir, Mrs Asmah, Mr Azmi, Mrs Mariam and others for their co-operation. To my friends, Hasliza Bahruji, Azmi, Suhaila, Hasmariza, Wong Kah Man, Lau Chin Guan, thank you for your support.

Finally, very thankful to my parents, my parents in law, my husband and my beloved daughter for their love, understanding, encouragement and support.

ABSTRACT

Zeolites are widely used as acid catalysts for the synthesis of fine chemicals in industrial processes. One such process is Friedel-Crafts alkylation which proceeds in the presence of acid catalysts. In this research, the acid property of zeolite Beta was studied in order to increase its activity in the Friedel-Crafts alkylation of resorcinol with *tert*-butanol. Zeolite Beta was chosen as catalysts in the Friedel-Crafts alkylation because it possesses large pore and high acid strength. Zeolite Beta was modified by varying the SiO_2/Al_2O_3 ratios of the initial gel and introducing niobium oxide into zeolite Beta samples. All samples were characterized by XRD, FTIR, N_2 adsorption, UV-Vis DR and ^{29}Si MAS NMR. XRD results showed all samples gave highly pure zeolite Beta phase. ^{29}Si MAS NMR showed that the zeolite Beta samples with initial SiO_2/Al_2O_3 ratios = 27, 45 and 90 result in the zeolite Beta having Si/Al framework ratios of 11, 21 and 19 respectively. The crystallinity of zeolite Beta is slightly decreased after the introduction of niobium oxide into the samples. UV-Vis DR results showed that the niobium species in zeolite Beta samples are mainly in the tetrahedral form. Acidity study of the catalysts was measured by FTIR pyridine adsorption and TPD of ammonia. FTIR pyridine showed that the amount of Brönsted acid sites in zeolite Beta samples increased in the order of framework Si/Al ratios = 21 < 19 < 11 and also increased after 2 % wt Nb loading but decreased after 4 % Nb loading. Meanwhile the Lewis acid site did not showed any correlation to the Si/Al ratios of zeolite Beta but increased after incorporated with niobium. TPD results showed that the amount of acid sites in zeolite Beta samples decreased while the acid strength increased with the increased of Si/Al ratios of zeolite Beta framework. The strength and the amount of acid sites also increased after 2 % wt Nb loading and decreased after 4 % wt Nb loading. All catalysts were tested in Friedel-Crafts alkylation of resorcinol with *tert*-butanol. GC analysis showed the alkylation of resorcinol over zeolite Beta at different Si/Al ratios produced 4,6-di-*tert*-butylresorcinol (main product) and 4-*tert*-butylresorcinol. The conversion decreased in the order, zeolite Beta with Si/Al = 11 (95 %) > 19 (70 %) > 21 (64 %) and the selectivity of 4,6-di-*tert*-butylresorcinol also decreased in the order Si/Al= 11 (81 %) > 19 (78 %) > 21 (56 %). Zeolite Beta sample with Nb loading has successfully produced 4,6-di-*tert*-butylresorcinol with 100 % selectivity. ESR analysis showed that the alkylation product containing butylated resorcinol is 4 times stronger antioxidant than the resorcinol itself.

ABSTRAK

Zeolit telah digunakan secara meluas sebagai mangkin asid untuk sintesis bahan kimia dalam proses industri. Satu contoh proses ialah pengalkilan Friedel-Crafts dengan bermangkinkan asid. Dalam kajian ini, sifat keasidan zeolit Beta telah dikaji untuk meningkatkan aktivitinya dalam tindak balas pengalkilan Friedel-Crafts antara resorsinol dan *tert*-butanol. Ia dipilih kerana mempunyai liang yang besar dan tapak asid yang kuat. Zeolit Beta telah diubahsuai dengan mempelbagaikan nisbah SiO_2/Al_2O_3 campuran gel awal dan memasukkan niobium oksida kedalam sampel zeolit Beta. Semua sampel telah dicirikan dengan kaedah XRD, FTIR, penjerapan nitrogen, UV-Vis DR dan ^{29}Si MAS NMR. Hasil XRD menunjukkan semua sampel mempunyai ketulenan fasa zeolit Beta yang tinggi. Hasil ^{29}Si MAS NMR menunjukkan sampel zeolit Beta dengan nisbah awal SiO_2/Al_2O_3 = 27, 45 dan 90 masing-masing menghasilkan zeolit Beta dengan nisbah bingkaian Si/Al = 11, 21 dan 19. Kehabluran sampel zeolit Beta berkurang sedikit setelah ditambah niobium oksida. Hasil UV-Vis DR menunjukkan spesies niobium dalam sampel zeolite Beta sebahagian besarnya adalah dalam bentuk tetrahedron. Kajian terhadap keasidan mangkin telah diukur menggunakan kaedah penjerapan piridina-FTIR dan ammonia TPD. Hasil penjerapan piridina-FTIR menunjukkan jumlah tapak asid Brönsted dalam sampel zeolit Beta bertambah mengikut urutan nisbah bingkaian Si/Al = 21 < 19 < 11 dan juga bertambah selepas dimuatkan dengan 2 % w/w Nb dan berkurang selepas dimuatkan dengan 4 % w/w Nb. Sementara itu, tapak asid Lewis tidak menunjukkan wujudnya sebarang korelasi terhadap nisbah Si/Al tetapi bertambah selepas dimuatkan dengan niobium. Hasil TPD menunjukkan jumlah tapak asid dalam sampel zeolit Beta berkurang sementara kekuatan tapak asid bertambah dengan pertambahan nisbah Si/Al dalam bingkaian zeolit Beta. Kekuatan dan jumlah tapak asid juga bertambah selepas dimuatkan dengan 2 % w/w Nb dan berkurang selepas dimuatkan dengan 4% w/w Nb. Semua mangkin diuji dalam tindak balas pengalkilan Friedel-Crafts antara resorsinol dan *tert*-butanol. Analisis KG menunjukkan pengalkilan resorsinol menggunakan zeolit Beta yang berbeza nisbah Si/Al telah menghasilkan 4,6-di-*tert*-butilresorcinol (hasil utama) dan 4-*tert*-butilresorcinol. Peratus pertukaran resorcinol berkurang mengikut urutan, zeolit Beta dengan nisbah Si/Al = 11 (95 %) > 19 (70 %) > 21 (64 %) dan peratus kepilihan 4,6-di-*tert*-butilresorcinol juga berkurang mengikut urutan nisbah Si/Al= 11 (81 %) > 19 (78 %) > 21 (56 %). Sampel zeolite Beta yang mengandungi Nb telah berjaya menghasilkan 4,6-di-*tert*-butilresorcinol dengan kepilihan 100 %. Analisis ESR menunjukkan produk pengalkilan yang mengandungi butil resorcinol mempunyai sifat antioksida 4 kali lebih kuat daripada resorcinol sendiri.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS / ABRREVIATIONS

BEA-11	Zeolite Beta with Si/Al=11 ratio in zeolite framework
BET	Brunnauer,Emmet and Teller
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
2,4-DTBP	2,4-di *tert*-butylphenol
D4R	Double 4 ring
D6R	Double 6 ring
DPPH	1,1-Diphenyl-2-picryl-hydrazyl
ESR	Electron Spin Resonance
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
H-BEA	Zeolite Beta in hydrogen form
Nb	Niobium
2Nb-BEA-11	Zeolite Beta (Si/Al=11) with 2 % niobium loading
PBU	Primary Building Unit
RHA	Rice Husk Ash
SBU	Secondary Building Unit
Si-27	Zeolite Beta with SiO_2/Al_2O_3= 27
^{29}Si MAS NMR	^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance
TEAOH	Tetraethylammonium hydroxide
TPD-Ammonia	Temperature Programmed Desorption of Ammonia
UV-Vis DR	Ultra Violet - Visible Diffuse Reflectance
wt %	Weight %
XRD	X-Ray Diffractogram

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Chemical process industry is a large industry with a global turnover of US $1400 billion per year (Roland and Kleinschmit, 1996). It has been recognized that the status of chemical process industry is a reliable indicator of the country's state of industrialization. It is well known that the chemical process industry is mainly based on catalytic processes. More than 90% of all chemical products manufactured involve at least one catalytic step, mostly even several catalytic procedures (Hölderich *et al.,* 1997). Zeolite acid catalysts have a wide application in industrial processes such as alkylation, isomerization, amination, cracking and etc (Tanabe and Hölderich, 1999). According to them, zeolites are the highest number of catalyst used in industrial processes. The utilization of zeolites as catalysts in industrial processes occupies 40%, followed by the oxides, complex oxides and ion-exchange resins.

The ability of zeolites as catalysts in organic processes has been investigated by many researchers. Zeolite Beta is a typical example of the zeolite with high activity in fine chemical reactions. Zeolite Beta has proven to be a reactive acid catalyst in many organic processes such as alkylation (Cheralathan *et al.,* 2003; Chiu *et al.,* 2004), acylation (Casagrande *et al.,* 2000) and various hydrocarbon reactions (Absil and Hatzikos, 1998). Zeolites are employed as an alternative heterogeneous catalyst instead of homogeneous catalysts particularly in Friedel-Crafts reaction since it is more efficient and environmentally-friendly which can eventually reduce plant corrosion and eliminate environmental problems. The key opportunity for the use of zeolites as catalysts relies on their unique pores which can control the selectivity of the reaction. Zeolites possess acid sites on the surface which can catalysed reaction such as Friedel-Crafts. The acid sites in zeolites are linked to tetrahedral aluminium atoms in the framework of the zeolite (Zaiku *et al.,* 2002). Therefore the acidity depends on the amount of aluminium framework.

1.2 Research Background

Friedel-Crafts alkylation of aromatics is one of the most significant basic reaction in organic chemistry and of great importance in synthesizing fine chemicals. Some of these chemicals are used in the production of antioxidants (Narayanan and Murthy, 2001; Zhang *et al*., 1998), intermediates for polyester fibers, engineering plastics, and liquid crystalline polymers for electronic and mechanical devices and films (Ahedi *et al.,* 2003). More specifically, the alkylation of resorcinol with *tert*-butanol is a reaction of practical interest since it produces butyl resorcinol which has potential uses as antioxidants, polymer stabilizers and in the treatment of mitochondrial respiration ailments (Narayanan and Murthy, 2001).

In general, Friedel-Crafts reaction is carried out with classic Lewis acid catalyst such as $AlCl_3$, BF_3 and $TiCl_4$, coupled with strong mineral acids such as HF and H_2SO_4, $Cu(OTf)_2$ and $Sn(OTf)_2$ (Chandra *et al.,* 2002). However the present use of conventional Lewis acid catalysts such as $AlCl_3$ courses a number of problems. First, the use of greater than stoichiometric amounts of the catalyst are needed, due to the configuration of a complex between the product and the catalyst. Second, the following hydrolysis of the catalysts leads to the loss of the catalyst as well as the problem of the disposal of the catalyst which consequently affects the environment. Therefore, heterogeneous catalysts have been chosen to replace the homogeneous catalysts in Friedel-Crafts reaction. The use of zeolites and other solid acid catalysts as heterogeneous catalysts in the manufacture of chemical intermediates and fine chemicals is gaining much more attention in recent years (Tanabe and Hölderich, 1999).

In this research, we have chosen zeolite Beta to be studied as the catalyst, following the current development in heterogeneous catalysis in Friedel-Crafts reaction. Zeolite Beta has great potential industrial interest because of its high acidity, large pore (5.0-7.0 Å) and peculiar pore systems and high silica content and has a high thermal stability. It is well known that zeolite possesses both Brönsted and Lewis acid sites. The acidity of a zeolite is one of the most important topics in the study of zeolite catalysis. The acid sites in zeolites are linked to the tetrahedral aluminium atoms in the framework of the zeolite (Zaiku *et al.,* 2002). Studies have shown that the amount of Brönsted and Lewis acid determine the selectivity of Friedel-Crafts reaction (Narayanan and Muthy, 2001; Narayanan and Sultana, 1998; Nivarthy *et al.,* 1998; Yadav and Doshi, 2003). Therefore, in this study the acidity of zeolite Beta will be modified by varying the Si/Al ratio of the framework as well as introducing niobium oxides as a support metal into zeolite Beta lattice.

1.3 Research Objectives

The objectives of this study are:

1) To synthesize zeolite Beta at different Si/Al ratios.
2) To modify the acidity of zeolite Beta by introducing niobium oxide
3) To determine the acidity of the modified zeolite beta.
4) To test the reactivity of the catalysts in Friedel-Crafts alkylation of resorcinol with *tert*-butanol.

1.4 Scope of Research

In this research, zeolite Beta was first synthesized using white rice husk ash (RHA) as silica sources. Zeolite Beta was synthesized with various SiO_2: Al_2O_3 molar ratios of the initial gel to obtain zeolite Beta with different Si/Al ratios framework. The acidity of zeolite Beta was further modified by introducing niobic acid as niobium oxide precursor through wet impregnation method.

The characterization of the catalysts was performed by using appropriate techniques which include powder X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), ^{29}Si Magic Angle Spinning (MAS) NMR spectroscopy, UV-Visible Diffuse Reflectance spectroscopy (UV-Vis DR) and nitrogen adsorption-desorption measurement. The acidity measurement of the prepared zeolite Beta catalysts was carried out by Temperature Programmed Desorption (TPD) of ammonia method and pyridine adsorption monitored by Fourier Transform Infrared spectroscopy (FTIR).

The final part in this study was to test the catalytic activity of the prepared catalysts in Friedel-Crafts alkylation of resorcinol with *tert*-butanol. The comparison of reactivity and selectivity of the catalysts in the Friedel-Crafts alkylation has been made between unmodified zeolite Beta and modified zeolite beta. The reaction was performed in a batch reactor and the product was analysed by gas chromatography (GC) while the identification of the products was carried out by using Gas Chromatography-Mass Spectrometry (GC-MS). Lastly, the study of antioxidant properties of the Friedel-Crafts reaction product was conducted by reacting the sample with 1,1-diphenyl-2-picryl-hydrazyl (DPPH) radical and the activity was measured using Electron Spin Resonance (ESR) method.

REFERENCES

Absil, R. P. L. and Hatzikos, G. H. (1998). *Hydrocarbonn Conversion Process Using Zeolite Beta Catalysts.* (U.S. Patent. 5, 833-840).

Ahedi, R. K., Tawada, S., Kubota, Y., Sugi, Y., and Kim, J. K. (2003). Shape-selective alkylation of biphenyl catalyzed by H-[Al}-SSZ-31 zeolite. *Journal of Molecular Catalysis A: Chemical.* 197: 133-146.

Ahmad, I., Dines, T. J., Anderson, J. A., and Rochester, C. H. (1999). Fourier-transform infrared study of the adsorption of acetophenones on niobic acid. *Spectochimica Acta Part A.* 55: 397-409.

Aguilar, J., Corma, A., Melo, F.V., Sastre, E. (2000). Alkylation of biphenyl with propylene using acid catalysts. *Catalysis Today*. 55: 225-232.

Algarra, F., Corma, A., Garcia, H., and Primo, J. (1995) Acid zeolites as catalysts in organic reactions. Highly selective condensation of 2-alkylfurans with carbonylic compounds. *Applied Catalysis A: General.* 128: 119-126.

Anonymous. (1996). *US Zeolite Market Set to Reach $1 Billion in 2001, Study Says*. Chemical Market Reporter. New York: Schnell Publishing Company.

Anonymous, (2001).*D458: Zeolite: Industry Trends and Worlwide Markets in 2010*. Frost & Sullivan.

Armaroli, T., Busca, G., Carlini, C., Giuttari, M., Galletti, A. M. R., and Sbrana, G. (2000). Acid sites characterization of niobium phosphate catalysts and their activity in fructose dehydration to 5-hydroxymethyl-2-furaldehyde. *Journal of Molecular CatalysisA: Chemical.* 151: 233-243.

Armengol, E., Corma, A., Garcia, H., and Primo, J. (1995). Acid zeolites as catalysts in organic reactions. Chemoselective Friedel-Crafts alkylation of benzene and toluene with cinnamyl alcohol. *Applied Catalysis A: General.* 126: 391-399.

Bagnasco, G. (1996). Improving the Selectivity of NH_3 TPD measurements. *Journal of Catalysis.* 159: 249-252.

Bajpai, P. K. (1986). Synthesis of mordenite type zeolite. *Zeolites.* 6: 2-8.

Barrer, R. M. (1982). *Hydrothermal Chemistry of Zeolites.* London: Academic Press.

Barthel. N., Finiels, A., Moreau, C., Jacquot, R., and Spagnol, M. (2001). Kinetic study and reaction mechanism of the hydroxyalkylation of aromatic compounds over H-BEA zeolites. *Journal of Molecular catalysis A Chemical.* 169: 163-169.

Bergman, M., Perelman, A., Dubinsky, Z., and Grossman, S. (2003). Scavenging of Reactive Oxygen Species by a Novel Glucurinated Flavonoid Antioxidant Isolated and Purified from Spinach. *Phytochemistry*. 62: 753-762.

Bhat, R. N., and Kumar, R. (1990). Synthesis of Zeolite Beta Using Silica Gel as a Source of SiO_2. *J. Chem. Biotechnology*. 48: 453-466.

Biju, M. D., Halligudi, S. B., Elangovan, S. P., Ernst, S., Hartmann, M., and Lefebvre, F.,. (2004). Zirconia supported phosphotungstic acid as an efficient catalyst for resorcinol *tert*-butylation and *n*-heptane hydroisomerization. *Journal of Molecular Catalysis A:Chemical.* 221: 113-119.

Breck, D. W. (1974). *Zeolite Molecular Sieves, Structure, Chemistry and Use*. New York: John Wiley and Sons.

Borade, R. B., and Clearfield, A. (1996). Preparation of Aluminium –rich Beta Zeolites. *Microporous Materials*. 5: 289-297.

Borade, R. B., and Clearfield, A. (1992). Characterization of Acid Sites in Beta and ZSM-20 Zeolites. *J. Physical Chemistry*. 96: 215-223.

Bourgeat-Lami, E., Massiani, P., Di Renso, F., Espiau, P., and Fajula, F. (1991). Study of the State of Aluminium in Zeolite β. *Applied Catalysis A*. 72: 139-152.

Camblor, M.A., Corma, A., and Valencia, S., (1997). Characterization of nanocrystalline zeolite Beta. *Microporous and Mesoporous Materials* 25: 59-74.

Camiloti, A.M., Jahn, S.L., Velasco, N.D., Moura, L. F., Cardoso, D. (1999). Acidity of Beta zeolite determined by TPD of ammonia and ethylbenzene disproportionation. *Applied Catalysis A: General.* 182: 107-113.

Cannan, T. R., and Hinchey, R. J. (1992). *Synthesis of Zeolite Beta*. (U.S. Patent 5, 139, 759).

Casagrande, M., Storaro, I., Lenarda, M., and Ganzerla, R. (2000). Highly Selective Friedel-Crafts Acylation of 2-metoxynaphthalene catalysed by H-BETA Zeolite. *Applied Catalysis A*. 201: 263-270.

Castro, D., Primo, C. J., and Corma, A. (1998). Heteropolyacids and Large Pore Zeolites as Catalysts in Acylation Reactions Using Unsaturated Organic acids as Acylating Agents. *J. Molecular Catalysis A*. 134: 215-222.

Chandra, K. L., Saravanan, P., Singh, R. K., and Singh, V. K. (2002). Lewis acid catalyzed acylation reactions: scope and limitations. *Tetrahedron* 58: 1369-1374.

Chang, Y. F., Somorjai, G. A., and Heinemann, H. (1994). An $^{18}O_2$ temperature-Programmed Isotope Exchange Study of Transition-Metal-Containing ZSM-5

Zeolites Used for Oxydehydrogenation of Ethane, *Journal of catalysis*. 154: 24-32.

Charles N. S. (1991). *Heterogeneous catalysis in industrial practise*. Second edition. McGraw-Hill Inc.

Chen, S. S., and Yeoh, A. K. (1992). Development of zeolite NaY from Rice Husk Ash. *Journal of Industrial Technology*. 2. SIRIM, Malaysia.

Cheralathan K. K., Kumar, I. S., Palanichamy, M., and Murugesan, V.(2003). Liquid phase alkylation of phenol with 4-hydroxybutan-2-one in the presence of modified zeolite HBEA. *Applied Catalysis A: General.* 241: 247-260.

Chiu, J. J., Pine, D. J., Bishop, S. T., and Chmelka, B. F. (2004) "Friedel-Crafts alkylation properties of aluminosilica SBA-15 meso/macroporous monoliths and Jamesoporous powders". Journal of Catalysis 221:400-412.

Chu, C.T. W., and Chang, C. D. (1985). Isomorphous Substitution in Zeolite Framework. 1. Acidity of Surface hydroxyl in [B]-, [Fe]-, [Ga]-, and [Al]-ZSM-5. *Journal Physical Chemistry.* 89: 1569-1582.

Corma, A., Climent, M. J., Garcia, H., and Primo, J. (1989). Design of Synthetic Zeolites as Catalysts in Organic Reactions. Acylation of Anisole by Acyl Chlorides or Carboxylic Acids over Acid Zeolites. *Applied. Catalysis A.* 49: 109-123.

Costa, C., Dzikh,I. P., Lopes, J. M., Lemos, F., and Ribeiro, F. R. (2000). Activity-acidity relationship in zeolite ZSM-5. Application of Brönsted-type equations. *Journal of Molecular Catalysis A: Chemical.* 154: 193-201.

Cullity, B. D.(1956). *Elements of X-ray Diffraction*. Second edition. Adison-Wisley Publishing Co.

Damyanova, S., Dimitrov, L., Petrov, L. and Grange, P. (2003). Effect of niobium on the surface properties of Nb_2O_5-SiO_2-supported Mo catalysts. .*Applied Surface Science.* 214: 68-74.

Das, D., and Cheng, S. (2000). Friedel-Crafts acylation of 2-methoxynaphtalene over zeolite catalysts. *Applied Catalysis A: General.* 201: 159-168.

Diaz-Mendoza, F. A., Pernett-Bolano, L., and Cardona-Martinez, N. (1998). Effect of Catalysts deactivation on the acid properties of zeolite used for isobutene/butane alkylation. *Thermochimica Acta.* 312: 47-61.

Didik, P. (2001). *Pengoptimuman sintesis zeolite beta daripada abu sekam padi:pencirian dan tindakbalas pemangkinan Friedel-Crafts.* UTM. Tesis MSc.

Dutta, P. K., Rao, K. M., Kresge, C. T., and Kennedy G. J. (1994). Examination of the Growth Dynamic of Zeolites ZSM-5 and Mordenite From Inorganic Reactants Compositions. *Microporous and Mesoporous Materials.* 3: 17-27.

Eapen, M. J., Reddy, K. S. N., and Shiralkar, V. P. (1994). Hydrothermal Crystallization of Zeolite Beta Using Tetraethylammonium Bromide. *Zeolites.* 14: 295-302.

Engelhardt, G. and Michael, D. (1987). "High-Resolution Solid-State NMR of Silicates and Zeolites." Chichester: John Wiley & Sons.

Escola J. M., and Davis M. E. (2001). Acylation of biphenyl with acetic anhydride and carboxylic acids over zeolite catalysts. *Applied Catalysis A: General.* 214: 111-120.

Fierro, J.L.G. (1990). "Spectroscopic Characterization of Heterogeneous Catalysts, part A: Methods of Surface Analysis." Amsterdam: Elsevier Science Publishers B.V

Feller, A., Guzman, A., Zuazo, I., and Lercher, J.A. (2004). On the mechanism of Catalyzed Isobutanol/butane alkylation by Zeolites. *Journal of Catalysis.* 224: 80-93.

Flanigen, E.M. (1991). "Zeolite and Molecular Sieve An Historical Perspective," in Bekkum, H.V., Flanigen, E.M. and Jansen, J.C. "Introduction to Zeolite Science and Practice, Studies in Surface Science and Catalysis." 58. Amsterdam: Elsevier.

Flanigen, E.M. (1976). Structural Analysis by Infrared Spectroscopy, in Zeolite Chemistry and Catalysis. In Rabo, J.A, *Zeolite Chemistry and Catalysis*. ACS *Monograph.* 171: 80-117.

Francisco J. M., Carmen M. L., Maria, A. C., and Caribary, U. (1999). Template Free Synthesis and Catalytic Behaviour of Aluminium Rich MFI-Type Zeolites. *Applied Catalysis A: General.* 181: 29-38.

Francisco, M. S. P., Landers, R., and Gushikem, Y. (2004). Local order structure and surface acidity properties of a Nb_2O_5/SiO_2 mixed oxide prepared by the sol gel processing method. *Journal of Solid State chemistry.* 177: 2432-2439.

Gallo, J. M.R., Paulino, I. S., and Schuchardt, U. (2004). Cyclooctene epoxidation using Nb-MCM-41 and Ti-MCM-41 synthesized at room temperature. *Applied Catalysis A: general.* 266: 223-227.

Gao, X., Wachs, I. E., Wong, M. S., and Ying, J. Y. (2001). Structural and Reactivity Properties of Nb-MCM-41: Comparison with That of Highly Dispersed Nb_2O_5/SiO_2 Catalysts. *Journal of Catalysis.* 203: 18-24.

Gregg, S. J., and Sing, K. S. W. (1982). *Adsorption, Surface Area and Porosity*. 2nd. Ed. London: Academic Press.

Gunnewegh, E.A., Gopie, S. S., and Bekkum, H. V. (1996). H MCM-41 Type Molecular Sieves as Catalysts for Friedel-Crafts Acylation of 2-metoxynaphtalene. *J. Molecular. Catalysis A*. 106: 151-158.

Gunnewegh. E. A., Hoefnagel A. J., and Bekkum, H. V. (1995). Zeolite catalysed synthesis of coumarin derivatives. *Journal of molecular Catalysis A: Chemical* 100: 87-92.

Halgeri, A. B. and Das, G. (1999). Novel catalytic aspects of beta zeolite for alkyl aromatics transformation. *Applied Catalysis A: General.* 181: 347-354.

Hamdan, H., Ramli. Z., Endud, S., Chinnapan, S. M., Yan, S. S. and Chew, W. K. (2000). Sintesis dan Pencirian Zeolit Beta daripada Silika Sekam Padi. UTM. *Buletin Kimia.* 15: 37-44.

Han, M., Lin, S., and Roduner, E.(2003). Study on the alkylation of benzene with propylene over Hβ zeolite. *Applied catalysis A: General.* 243: 175-184.

Higgins, J. B., La Pierre, R. B., Schlenker, J. L., Rohrman, A. C., Wood, J. D., Kerr, G. T. and Rohrbaugh, W. J. (1998). The Framework Topology of Zeolite Beta. *Zeolites.* 8: 446 - 452.

Hedge, S. G., Kumar, R., Bhat, R. N. and Ratnasamy, P. (1989). Characterization of the Acidity of Zeolite Beta by Ftir Spectroscopy and TPD of NH_3. *Zeolites.* 9: 231-237.

Hölderich, W. F., Röseler, J., Heitmann, G., and Liebens, A. T. (1997). The use of zeolites in the synthesis of fine and intermediate chemicals. *Catalysis Today*. 37: 353-366.

Hunger B., Heuchel, M., Clark, L. A., and Snurr, R. Q. (2002). Characterization of Acidic OH Groups in Zeolites of Different Types: An Interpretation of NH_3-TPD Results in the Light of Confinement Effects. *Journal Physical Chemistry B.* 106: 3882-2889.

James, J.and Rao, M. S.(1986) Characterization of Silica in Rice Husk Ash. *American Ceramic Society Bulletin*.65: 1177-1180.

Jansen, J. C., Creighton, E. J., Njo, S. L., Koningsveid, H. and Bekkum, H. V. (1997). On the Remarkable Behavior of Zeolite Beta in Acid Catalysis. *Catalysis Today*. 38: 205 - 212.

Juttu, G. (2001). *Modified Microporous Aluminosilicates As Novel Solid Acid Catalysis*. University of Delaware. Ph.D Thesis.

Je, J. Y., Park, P. J., and Kim, S. K. (2004). Free radical scavenging properties of hetero-chitooligosaccharides using an ESR spectroscopy. *Food and Chemical Toxicology.* 42: 1-7.

Jehng, J. M., and Wachs, I. E. (1993). Molecular Design of Supported Niobium Oxide Catalysts.*Catalysis Today.* 16: 417-426.

Jia, D., Massiani, P., and Barthomeuf, D. (1993). Characterization by Infrared and Nuclear Magnetic Resonance Spectroscopies of Calcined Beta Zeolite. *J. Chem.Soc*. *Faraday Trans*. 89: 3659-3665.

Jin, Z.Q., and Chen, X. (1998). A Simple Reproducible Model of Free Radical Injured Isolated Heart Induced by 1,1-Diphenyl-2-Picryl-Hydrazyl (DPPH). *Journal of Pharmacological and Toxicological Methods.* 39: 63-70.

Kapur, T., Kandpal, T. C., and Garg, H. P. (1998). Electricity Generate from Rice Husk in Indian Rice Mills: Potential and Financial Viability. *Biomass Energy.*14: 573-583.

Kim, S. D., Lee, K. H., Jae S. L.,Yong G. K. and Kwang E.Y. (2000). “The Regioselective Acylation of 2-methoxynaphthalene to 2-acetyl-6-methoxynaphthalene over Zeolite Beta” *Molecular Catalysis A.* 152: 33-45.

Kiricsi, I., Flego, C., Pazzuconi, G., Parker J.W. O., Millini, R., Perego, C., and Bellussi, G. (1994). Progress Toward Understanding Zeolite β Acidity:An IR and ^{27}Al NMR Spectroscopy Study. *J.Physical Chemistry*. 98: 4627-4634.

Kuehl, G. H., and Timken, H. K. C. (2000). Acid Sites in Zeolite Beta: Effects of Ammonium Exchange and Steaming. *Microporous and Mesoporous Materials*. 35: 521-532.

Listiorini, E., Ramli, Z., and Hamdan, H.(1996) “Optimization and Reactivity study of Silica in The synthesis of zeolites from Rice Husk Ash.” *J. Teknologi.*25: 27-35.

Louli, V., Ragoussis, N., and Magoulas, K. (2004). Recovery of phenolic antioxidants from wine industry by-products. *Bioresource Technology*. 92: 201-208.

Maheswari, R., Gore K.U., and Tope, B.B. (2003). Tertiary butylation of Phenol over HY and dealuminated HY zeolites. *Journal of Molecular Catalysis A: Chemical* 193: 251-257.

Meier, W.M., Olson, D. H., and Boerlocher, C. (1996). *Atlas of Zeolite Structure types*. 4th edition Amsterdam: International Zeolite Association.

Mendes, F. M. T., Perez, C. A., Soares, R. R., Noronha, F. B., and Schmal, M. (2003). Ammonium complex of niobium as a precursor for the preparation of Nb_2O_5/Al_2O_3 catalysts. *Catalysis Today.* 78: 449-458.

Mitra, A., Subramanian, S., Das, D., Satyanarayana, D., Chilukuri, V. V. and Chakrabarty, D. K. (1997). Alkylation of aromatics on zeolite beta. Unusual butylation of benzene with isobutanol. *Applied Catalysis A: General.* 153: 233-241.

Miyamoto, Y., Katada, N., and Niwa, M. (2000). Acidity of β zeolite with different Si/Al_2 ratio as measured by temperature programmed desorption of ammonia. *Microporous and Mesoporous Materials*. 40: 271-281.

Murphy, M. S. (1996). *Structural Modification of Zeolite Beta.* University OF New Brunswick. Master Thesis.

Moraes, M., Pinto, W. D. S. F., Gonzalez, W. A., Carmo, L. M. P. M. Pastura, N.M.R., and Lachter, E. R. (1996). Benzylation of toluene and anisole by benzyl alcohol catalyzed by niobic acid: influence of pretreatment temperature in the catalytic activity of niobic acid. *Applied Catalysis A:General.* 138: L7-L12.

Muller, M., Harvey, G. and Prins, R. (2000). Quantitative Multinuclear MAS NMR studies of zeolites. *Microporous and mesoporous materials.* 34: 281-290.

Nakamoto, K. (1962). *Infrared and raman Spectra of Inorganic and Coordination Compounds.* A Wiley Interscience Publication- John Wiley & Sons.

Narayanan, S., and Deshpande, K. (1995). Mechanism of aniline alkylation over vanadia and supported vanadia. *Journal of Molecular Catalysis A: Chemical.* 104: L109-L113.

Narayanan, S., and Deshpande, K. (2000). Aniline alkylation over solid acid catalysts. *Applied Catalysis A: General.* 199: 1-31.

Narayanan, S., and Sultana, A. (1998). Aniline alkylation with ethanol over zeolites and vanadium modified zeolites prepared by solid state exchane method. *Applied Catalysis A: General.* 167: 103-111.

Narayanan, S., and Murthy, K.V.V.S.B.S.R. (2001). Montmorillonite as a versatile solid acid catalyst for *tert*-butylation of resorcinol. *Applied Catalysis A: General* 213: 273-278.

Nivarthy, G. S., Seshan, K., and Lercher, J. A. (1998). The influence of acidity on zeolite H-BEA catalyzed isobutene/n-butene alkylation. *Microporous and Mesoporous Material.* 22: 379-388.

Nowak, I. and Ziolek, M. (1999). Niobium compounds: Preparation, Characterization, and Application in Heterogeneous catalysis. *American Chemical Society.* 99: 3603-3624.

Olah, G.A. (1973). *Friedel-Crafts Chemistry*. New york: John Wiley and sons.

Pariente, J. P., Martens, J. A., and Jacobs, P. A. (1988). Factor Affecting the Synthesis Efficiency of Zeolite Beta from Aluminosilicate Gels Containing Alkali and tetraethylammonium Ions. *Zeolites.* 8: 46-53.

Pariente, J. P., Martens, J. A. and Jacobs, P. A. (1987). Crystallization Mechanism of Zeolite Beta from TEA_2O, Na_2O and K_2O Containing Silicates Gels. *App. Cat. A.* 31: 35 – 64.

Roland, E., P. Kleinschmit, P. (1996). *Ullman's Encyclopedia of Industrial Chemistry:* VCH Verlagsgesellschaft. Vol A28: 475-504.

Rehman, Z. and Salariya, A.M. (2006). Effect of synthetic antioxidants on storage stability of Khoa-a semi-solid concentrated milk product. *Food Chemistry*. 96:122-125.

Resini, C., Panizza, M., Raccoli, F., Fadda, M., Maria, M., Carnasciali, M., Busca, G., Lopez, E. F., and Escribano, V. S. (2003). Oxidation of ethane and cyclohexane over vanadia-niobia-silica catalysts. *Applied Catalysis A: General.* 251: 29-38.

Shi, Y. F., Gao, Y., and Yuan, W. K. (2002). Some characterization of β-zeolite foralkylation of benzene in near critical regions. *Catalysis today.* 74: 91-100.

Suzuki, K., and Hayakawa, T. (2005). The effects of seeding in the synthesis of zeolite ZSM-48 in the presence of tetramethylammonium ion. *Microporous and mesoporous materials.* 77: 131-137.

Szostak. R. (1989). *Molecular Sieves: Principles of synthesis and Identification*. Van Nostrand Reinhold catalysis series, New York.

Tanabe, T., and Hölderich, W. F. (1999). Industrial application of solid acid-base catalysts. *Applied Catalysis A: General.* 181: 399-434.

Tanabe, K., and Okazaki, S. (1995). Various reactions catalyzed by niobium compounds and materials. *Applied Catalysis A: General.* 133: 191-218.

Tanaka, T., Nojima, H., Yoshida, H., Nakagawa, H., Funabiki, T., and Yoshida, S. (1993). Preparation of highly dispersed niobium oxide on silica by equilibrium adsorption method. *Catalysis Today.*16: 297-307.

Tao, K., Li, W., Li, H., and Qi, X. (1996). Effect of modified industrial zeolite beta on one-step catalytic hydration of propene to isopropanol. *Applied Catalysis A: General.* 139: 43-49.

Treacy, M. M. J., Higgins, J. B., and Ballmoos, R. V. (1996). *Collection of Simulated XRD Powder Patterns for Zeolites*. 3rd edition. Amsterdam: Elsevier.

Trouillas, P., Calliste,C. A., Allais, D. P., Simon, A., Marfak, A., Delage, C., and Duroux, J. L. (2003). Antioxidant, anti-inflammatory and antiproliferative properties of sixteen water plant extracts used in the Limousin countryside as herbal teas. *Jurnal Food Chemistry.* 80: 399-407.

Ukeda, H., Adachi, Y., and Sawamura, M. (2002). Flow injection analysis of DPPH radical based on electron spin resonance. *Talanta*. 58: 1279-1283.

Wade, J. R. (2003). *Organic Chemistry*. 5th Edition. New Jersey. Prentice Hall, Pearson Education Inc.

Wadlinger, R. L., Kerr, G. T., and Rosinski, E. J. (1967). *Synthesis Zeolite Beta*. (U.S. Patent 3, 308, 069).

Yadav, G. D., and Doshi, N. S. (2003). Alkylation of aniline with methyl-*tert*-butyl ether (MTBE) and *tert*-butanol over solid acids: product distribution and kinetics. *Journal of Molecular Catalysis A: Chemical.* 194: 195-209.

Yang, C., and Xu, Q. (1997). States of Aluminium in Zeolite β and influence of Acidic or Basic Medium. *Zeolites*. 19: 404-410.

Yoshida, H., Tanake, T., Yoshida, T., Funabiki, T., and Yoshida, S. (1996). Control of the structure of niobium oxide species on silica by the equilibrium absorption method. *Catalysis Today.* 28: 79-89.

Zaiku, X., Jiaqing, B., Yiqing, Y., Qingling, C., and Chengfang, Z. (2002) .Effect of treatment with $NaAlO_2$ solution on the Surface Acid Properties of Zeolite β. *Journal of Catalysis* 205: 58-66.

Zainab, R. (1995). *Rhenium-Impregnated Zeolites: Synthesis, Characterization and Modification as Catalysts in the Metathesis of Alkenes*. UTM: Thesis of PhD.

Zainab, R., and Hasliza, B. (2003). Synthesis of ZSM-5 Type Zeolite using crystalline Silica of Rice Husk Ash. *Malaysian Journal of Chemistry.* 5: 048-055.

Zhang, K., Huang, C., Zhang, H., Xiang, S., Liu, S., Xu, D., and Li, H. (1998) Alkylation of phenol with *tert*-butyl alcohol catalysed by zeolite Hβ. *Applied Catalysis A: General.* 166: 89-95.

Zhang, C. X., Wu, H. and Weng, X.C. (2004). Two novel synthetic antioxidants for deep frying oils. *Food Chemistry.* 84: 219-222.

Zhao, X. S., Lu, M. G. Q., and Song, C. (2003). Immobilization of aluminum chloride on MCM-41 as a new catalyst system for liquid-phase isopropylation of naphthalene. *Journal of Molecular Catalysis A: Chemical.* 191: 67-74.

Ziolek, M. (2003). Niobium-containing catalysts-the state of the art. *Catalysis Today.* 78: 47-64.