



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS OF HIERARCHICAL NANOZEOLITES BETA AND ZSM-5
FOR GREEN DIESEL PRODUCTION VIA HYDRODEOXYGENATION**

MAHASHANON A/L ARUMUGAM

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By

MAHASHANON A/L ARUMUGAM

**Thesis Submitted to the School of Graduate Studies, Universiti
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Philosophy**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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December 2018

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The application of the conventional zeolites has been limited due to its large crystal size (micrometer) and also due to the microporosity (size < 2nm). Hence, this study has been conducted to produce enhanced nanozeolites to overcome the above mentioned limitations. Herein, two microporous nanozeolites namely Beta and ZSM-5 were synthesized via hydrothermal method. Moreover, the enhanced hierarchical nanozeolites have been produced via a green solvothermal approach with the following attributes such as narrow particle size distribution and appropriate mesopores. The synthesis was based on reducing the growth of zeolite crystals by surface silanization of zeolitic seeds using organosilane (hexadecyltrimethoxysilane) as a growth inhibitor. The activities of these nanozeolites and hierarchical nanozeolites were evaluated with catalytic hydroprocessing of oleic acid to green diesel by incorporating Ni metals on these supports. Moreover, extensive characterizations and initial rate investigation were conducted to determine the nature of acid sites and their structural-functional relationship in selective hydrodeoxygenation (HDO) of octanoic acid. The results showed hydrothermally synthesized nanozeolites were made of globular aggregates with broader particle size distributions (48-1273 nm for zeolite Beta) and (60-135 nm for zeolite ZSM-5). A much smaller and narrower distributions of globular aggregates of hierarchical nanozeolites are formed using solvothermal approach with sizes of 65–120 nm (for Beta using acetone) and 30-100 nm (for ZSM-5 using 1-decanol). These globular aggregates are actually made by quite smaller primary nanounits ranging 4–11 nm size. The hierarchical nanozeolites exhibited secondary porosity, especially larger mesopores found in zeolite Beta (with pore diameter 8.1 nm) due to efficient functionalization of HDTM in polar solvent environment (acetone). Whereas, moderate mesopores observed in zeolite ZSM-5 (with pore diameter 7.8 nm) caused by the alkoxylation of alcohol based solvent (1-decanol). Catalytic

hydroprocessing of oleic acid pointed out higher yields of 60% (consisting of straight and isomeric alkanes C₁₈ and C₁₇) obtained over the microporous nanozeolites than hierarchical nanozeolites at 350 °C and 50 bar pressure. This is due to high surface activities demonstrated by the larger external surface areas of microporous nanozeolites. In contrast, the recyclability test of catalysts revealed that hierarchical nanozeolites minimized catalyst deactivation as they were capable of retaining their activities, over 40% (for HZSM-5) and 20% (for HBEA) yields even regenerated after four cycles. As for the initial rate study, all the Ni/zeolite catalysts exhibited higher selectivity towards the octane over the heptane, indicating conversion of octanoic acid occurred preferably via HDO than decarbonylation (DCN) route. The selectivity of the HDO pathway was strongly influence by the Bronsted acid sites of the zeolites. The initial rate studies revealed small Ni metal particles and it's highly dispersibility over support facilitate high initial catalytic activity. The fatty acid substrate can be quantitatively hydrodeoxygenated to alkanes by cascade reaction on bifunctional catalysts based on Ni and an acidic zeolite. The findings of this study discovered more effective and benign way of producing nanozeolites with high external surface area and hierarchical porosity that provide remarkable HDO activity and better catalyst stability as compared to other commercial support catalysts.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS HIERARKI NANOZEOLIT BETA DAN ZSM-5 UNTUK PENGHASILAN DIESEL HIJAU MELALUI HIDROPENYAHOKSIGENAN

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Penggunaan zeolit konvensional terhad disebabkan oleh saiz kristal yang besar (mikrometer) dan juga berliang mikro (saiz $< 2\text{nm}$). Oleh yang demikian, kajian ini telah dijalankan untuk menghasilkan nanozeolit yang dipertingkatkan untuk menangani batasan yang disebutkan di atas. Di sini, dua nanozeolit berliang mikro iaitu Beta dan ZSM-5 telah disintesis melalui kaedah hidroterma. Selain itu, peningkatan hierarki nanozeolit yang dihasilkan melalui kaedah sintesis solvoterma hijau mempunyai ciri-ciri seperti taburan saiz zarah jurang kecil dan liang meso yang sesuai. Sintesis ini berdasarkan kepada pengurangan pertumbuhan kristal zeolit melalui silanisasi permukaan benih zeolitik dengan menggunakan organosilana (heksadeciltrimetoksilana) sebagai ejen perencat pertumbuhan. Aktiviti nanozeolit dan nanozeolit hierarki ini diuji dalam penukaran asid oleik kepada disel hijau melalui proses hidro bermangkin dengan penambahan logam nikel pada penyokong zeolit tersebut. Disamping itu, kajian terhadap pencirian secara terperinci dan kadar awal telah dijalankan untuk menentukan sifat nanozeolit dan tapak asid nanozeolit hierarki dan hubungan struktur-fungsi zeolit dalam hidropenyahoksigenan selektif (HDO) asid oktanoik. Hasil eksperimen menunjukkan zeolit yang disintesis dalam keadaan hidroterma ialah agregat bundar dengan taburan saiz zarah yang lebih lebar (48-1273 nm untuk zeolit Beta) dan (60-135 nm untuk zeolit ZSM-5). Agregat berbentuk bundar nanozeolit hierarki yang lebih kecil dan taburan yang lebih sempit terbentuk dalam saiz 65-120 nm (untuk Beta dengan menggunakan aseton) dan 30-100 nm (untuk ZSM-5 dengan menggunakan 1-dekanol). Agregat bundar ini sebenarnya dibuat daripada nanounit primer yang agak kecil dalam lingkungan 4-11 nm. Nanozeolit hierarki mempunyai liang sekunder, terutama liang meso yang lebih besar bagi zeolit Beta (dengan diameter 8.1 nm) kerana kecekapan fungsi HDTM dalam persekitaran pelarut berketub (aseton). Manakala, liang sekunder yang sederhana dapat diperhatikan dalam zeolit ZSM-5 (dengan diameter 7.8 nm) disebabkan oleh pengalkoksilan pelarut berasaskan alkohol (1-dekanol). Proses hidro bermangkin menggunakan asid oleik

menunjukkan hasil yang lebih tinggi sebanyak 60% (terdiri daripada alkana lurus dan isomer C₁₈ dan C₁₇) yang diperolehi daripada nanozeolit berliang mikro berbanding dengan nanozeolit hierarki pada suhu 350 °C dan 50 tekanan bar. Ini disebabkan oleh aktiviti permukaan yang tinggi yang ditunjukkan oleh luas besar permukaan luar zeolit nano yang berliang mikro. Walaubagaimanapun, ujian kebolehan kitar semula mungkin menunjukkan bahawa nanozeolit hierarki mengurangkan penyahaktifan pemangkin disebabkan kebolehan untuk mengekalkan aktiviti, lebih 40% (untuk HZSM-5) dan 20% (untuk HBEA) malah mampu untuk dijanakan semula selepas empat kitaran. Semua pemangkin Ni/ zeolit menunjukkan pemilihan yang lebih tinggi ke arah penghasilan oktana berbanding dengan heptana, menunjukkan penukaran asid oktanoik lebih mudah berlaku melalui HDO berbanding penyahkarbonan (DCN). Pemilihan mungkin sangat dipengaruhi oleh muatan asid dan tapak asid Bronsted zeolit. Kajian kinetik mendedahkan zarah Ni yang kecil dan tahap taburan yang tinggi diatas penyokong memudahkan kadar aktiviti awal pemangkin yang tinggi. Substrat asid lemak boleh dihidrogenoksigenkan secara kuantitatif kepada alkana dengan tindak balas berperingkat pada mangkin dwifungsi berdasarkan Ni dan zeolit berasid. Penemuan kajian ini adalah mengetahui cara yang lebih berkesan dan kurang berisiko dalam penghasilan nanozeolit dengan luas permukaan luaran yang tinggi dan kelengkapan hierarki yang memberikan aktiviti HDO yang tinggi dan kestabilan mungkin yang lebih baik berbanding mangkin penyokong sedia ada.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

ACS	American Chemical Society
AIP	Aluminium isopropoxide
APTMS	3-aminopropyltrimethoxysilane
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflectance
BA	Bronsted acid
¹³ C MAS NMR	Solid state carbon-13 magic angle spinning nuclear magnetic resonance
CHNS	Carbon hydrogen nitrogen sulphur
Conv	Conversion
DCM	Dichloromethane
DCO	Decarboxylation
DCN	Decarbonylation
DMAC	Dimethylacetamide
DMC	Dimethyl carbonate
DMPU	N, N'-Dimethylpropyleneurea
DO	Deoxygenation
DRIFT	Diffuse reflectance infrared fourier transform spectroscopy
DTG	Derivative thermogravimetric
EA	Ethyl acetate
ECHA	European Chemicals Agency
EDX	Energy dispersive X-ray
ESH	Environment, Safety & Health
EU	European Union
FAEE	Fatty acid ethyl ester
FAME	Fatty acid methyl ester
FCC	Fluidized catalytic cracking
FESEM	Field emission scanning electron microscope
FESEM-EDX	Field emission scanning electron microscope energy dispersive X-ray
FTIR	Fourier transform infrared spectroscopy
GC-FID	Gas chromatography flame ionization detector
GC-MS	Gas chromatography mass spectroscopy
GSK	GlaxoSmithKline
HBEA	Hydrogen form zeolite Beta
HC	Hydroconversion
HDO	Hydrodeoxygenation
HDS	Hydrodesulphurization
HDTM	Hexadecyltrimethoxysilane
HZSM-5	Hydrogen form zeolite ZSM-5
IBTES	Isobutyltriethoxysilane
ICP-OES	Induced coupled plasma – optical emission spectroscopy
IEA	International Energy Agency
IR	Infrared spectroscopy
IZS	International Zeolite Association
LA	Lewis acid

CHAPTER 1

INTRODUCTION

1.1 Research Background

Over the years, human life and ecological environment have been seriously affected by global warming and climate changes issues owing to the increase of greenhouse gases emission. Besides, increasing concern about oil scarcity, instability in world crude oil prices and the fact that civil war is mainly intense in oil producing countries have directed the research in finding alternative energy sources. The development of synthetic fuel and biofuel technologies using renewable sources has become crucial in recent years (Bu et al., 2012; Hahn-Hägerdal et al., 2006; Wang et al., 2011). Biomass has emerged as one of most important renewable sources for biodiesel production because of their vast proficiencies to meet the demands for all variety of energies including transportation fuels and high-value chemicals. Biomass is a carbon-based renewable sources that is available in abundance in nature and it comprises of all sort of natural raw matter of plants and animals' origins (Wang et al., 2012).

In last decades, various technologies have been developed to produce biofuel from the biomass as a substitute for petroleum based fuels. Bio-oil is the oxygenated compounds produced by the fast pyrolysis of biomass and it is considered to be potential substitute for the fossil fuel. The bio-oil as a fuel is recognized to be better choice because the bio-oil produces a negligible amount of nitrogen oxides (NO_x), sulphur dioxide (SO_2) and soot when it is combusted (He and Wang, 2012; Jacobson et al., 2013; Mortensen et al., 2011; Ruddy et al., 2014).

Till date ample number of process have been employed for the upgradation of bio-oil and among them hydrodeoxygenation (HDO) is considered to be the most effective method. HDO is a hydrogenolysis process that removes oxygen molecules from bio-oil in the form of water under high hydrogen pressure and temperature in the presence of a specific heterogeneous catalyst. The bio-oil that upgraded with HDO produces a fuel known as green fuel or renewable diesel. The structure of green fuel is mainly consisting of paraffin that is similar to those of petrodiesel. HDO has received a considerable attention in the oil and gas industries because the process can be easily performed at the existing refineries (Jacobson et al., 2013; Mortensen et al., 2011; Ruddy et al., 2014; Veriansyah et al., 2012).

The efficiency of the HDO reaction depends on the efficiency of the catalyst used as well as the reaction conditions. However, the challenge lies in designing competent catalyst due to the complex structure of the bio-oil. Noble metals such as Pt, Pd, Rh and Ru promoted on various supports are among the most commonly studied HDO catalysts (Gutierrez et al., 2009; Hong et al., 2014; Wang et al., 2011). These supported noble metal catalysts usually show excellent catalytic activity in terms of reactant conversion and also the selectivity towards the saturated hydrocarbons. The activity of HDO reaction is also significantly influenced by the type of supports employed. Due to the metal-support interactions, the catalytic activity of the catalyst can be simply tailor-made to target the preference product. Supports materials like activated carbon, SiO₂, TiO₂, ZrO₂ and zeolites exhibit a decent metal dispersion and also reasonable stability in HDO process (Bykova et al., 2012; Peng et al., 2013; Zhao & Lercher, 2012).

Zeolites are characterized as a microporous crystalline aluminosilicates that not only occur naturally but also produced industrially on a large scale. The zeolites that commonly synthesized are zeolites with a BEA and MFI structure. These microporous zeolites are extensively employed in various industrial processes namely catalysis, separation, adsorption, and etc. (Coronas, 2010). The salient feature of zeolites is that they possess both acid as well as the basic sites, which results in the dual property of the zeolites. The dual property of zeolites plays a predominant role in the catalysis process. The acidic nature of zeolites is due to the presence of Lewis acid (LA) and Bronsted acid (BA) sites. Whereas the basicity is due the basic framework oxygen with the negative charge (Murphy et al., 1996). Zeolite's extensive crystalline framework and the topological channel structure provides consistent absorption behavior towards the guest molecules. Their adjustable acidity and well-defined pore structure, make them highly active in a variety of reactions.

In recent years, synthesis of zeolite materials with improved molecular accessibility has gain an immense interest because of their remarkable performance as a catalyst. The accessibility to zeolites' active sites have been improved by various approaches such as synthesis of zeolite in nanosized (i.e growing crystal in confined space like carbon matrix and etc) (Yang et al., 2004) or prepared zeolite with a secondary porosity via post-treatment methods (i.e dealumination, desilication) (Corma et al., 1998; Groen et al., 2004) or soft templating method (Serrano et al., 2006). Many nanozeolites have been formerly synthesized by hydrothermal treatment. The size of crystal can also be controlled by optimizing the zeolite starting gel compositions (such as template concentration, water content and type of precursors) as well as the hydrothermal synthesis condition (such as crystallization temperature and aging time) (Cambor et al., 1991; Hu et al., 2010; Renzo, 1998)

A new terminology called "hierarchical" has been introduced for zeolites having more than one porosity (that is, zeolite containing both micropores and

mesopores or with macropores) or mixture of all three. The hierarchical zeolites display a reduced steric hindrance and diffusional restrictions, as well as more precise molecule sieving ability of zeolite crystals (Wang, 2013). Hierarchical nanozeolites with high crystallinity, enhanced surface area, porosity and catalytic activity have been successfully synthesized through soft template assisted method. The method is based on reducing the growth of zeolite crystals by perturbing the zeolitic surface with surface silanization agent (SSA) such as organosilanes (Serrano et al., 2006). The size and the morphology of the mesoporous zeolite can be precisely regulated by tuning the functional group of the grafting agent, their concentration and synthesis parameters of surfactant molecules. This strategy has been employed in the synthesis of many hierarchical zeolites with enhanced textural features and significantly improved catalytic properties, as in the case of zeolite ZSM-5, Beta and mordenite (Aguado et al., 2009; Aguado et al., 2008; Serrano et al., 2009; Serrano et al., 2008). Their distinctive property has inspired a rapid grow and wide application in biomass conversion and bio-oil upgrading.

Synthesis of hierarchical nanozeolites via solvothermal method demonstrates narrower and even particle size distribution of the zeolites nanoparticles. In this method, organic solvent has been introduced as the medium for zeolite surface functionalization and crystallization instead of water. The zeolite precursors become hydrophobic after the surface grafting process and thus highly dispersed in the organic phase. The aggregation of nanoparticles is drastically reduced as the crystallization of the functional group protected protozeolitic species occur in the organic phase, resulting in smaller and uniform size of nanozeolites. The crystal size of the hierarchical nanozeolites can be modified to some extent by changing the property of solvent (Vuong and Do, 2007).

1.2 Problem Statements

Production of high quality and sustainable fuel has always been a great challenge to mitigate the global warning issues and to meet the growing energy demand of the rising world population. Vegetable oils from renewable biomass source is considered as perfect triglyceride feedstock because of containing long chain fatty acids with 12-24 carbon atoms which is very convenient to get diesel range product. Nevertheless, vegetable oil has high water and oxygen content which leads to low heating value, pH, high viscosity and polarity, and poor thermal and chemical stability (Bu et al., 2012; He and Wang, 2012; Li et al., 2014; Ruddy et al., 2014). In order to overcome these limitations, bio-oil as a fuel is in need to be further upgraded.

Hydroconversion (HC) of triglycerides to renewable diesel has many advantages over other fuel upgrading techniques. This is because an aliphatic hydrocarbon product is formed which has high cetane number and is completely indistinguishable from petroleum based diesel fuel (Mohammad et al, 2013). Three plausible reaction routes that could take place during the HC of

triglycerides which are HDO, decarbonylation (DCN) and/or decarboxylation (DCO). The HDO process involves the removal of oxygen atom in the form of water when the feedstock reacts with hydrogen at temperature (200-400 °C) and pressure (2-14 MPa), producing the same number of carbon atoms as the parent triglyceride molecules. Meanwhile in the DCN and DCO, the oxygen is removed in the form CO and CO₂ and the primary product is hydrocarbon with one carbon less than the parent triglyceride. The synthesis of the highly selective HDO catalyst is very crucial because of its tendency to maintain high carbon efficiency in the end-product and produce water as a green by-product (Cristea et al., 2015; Huber et al., 2007; Kubička and Kaluža, 2010).

Till date, numerous catalysts have been explored for the HDO process in obtaining high selective diesel product with mild operating process. The most commonly used are supported noble catalyst and sulfurized or reduced metal catalysts. Sulfurized catalysts such as CoMo/Al₂O₃ and NiMo/Al₂O₃ are widely used in HDO since sulfidation generates active sites on the catalyst (Şenol et al., 2005). However, HDO using sulfided catalysts is less favorable due to the formation of sulphur contaminated products and the reduction of the activity as the sulfur leaches in the reaction (Liu et al., 2015). The noble metal catalysts including Pd, Pt, Ru, Rh and PtSn are not favorable because of their prone to poisoning and are relatively expensive (Zhang et al., 2013). Moreover, inappropriate selection of the supports having low surface area that limits the interaction of reactant molecules on the active sites of the dispersed metals can subsequently reduce the rate of reaction (Chiranjeevi et al., 2001; Dhar et al., 2003). Therefore, considerable attention must be given in developing an economically feasible catalyst with better catalytic performance and stability.

Zeolites are known to have high surface area, high crystallinity and larger internal pore volumes that makes them extraordinary in many catalytic reactions (Wang et al., 2013). In spite of these unique properties, zeolites have a major shortcoming to be used as catalyst especially in bio-oil upgrading. The relatively smaller and solely micropores present in the conventional zeolites is the major limitation because it restricts the to and fro transportation of large reactant molecules in the active site. Besides this, deactivation caused by the coke formation also continually limits the usage of zeolites as a catalyst in many catalytic reactions (Liu et al., 2014). Hence the researchers are in the urge to synthesize zeolites that are nanosized with large external surface area, high surface activity and hierarchical pore structured to overcome the above mentioned limitations (Chen et al., 2012).

In the past decades, various nanozeolite materials have been successfully synthesized by hydrothermal treatment. The synthesis parameters including gel composition, aging time, temperature and nature of the starting materials do have a significant contribution to the morphology of the crystals formed (Renzo, 1998). A modest change in this synthesis parameters using the clear gel method can lead to poorly crystalline zeolite and also leads to the formation of undesired

products (Cundy et al. 2003; Cundy and Cox, 2003). Therefore, it is very crucial to study the influencing factors under the hydrothermal treatment to achieve a fine control on the crystal size of nanozeolite. This synthesis strategy and interrelated results is expected to provide a solid foundation and fruitful idea prior to the synthesis of the hierarchical structured nanozeolites.

Preparation of mesoporous MFI and BEA zeolites with the addition of SSA agents to the raw gel, has significant impacts in generating the additional porosity in the structure and therefore improving the textural properties of the materials. The incorporation of the organosilane species on the external surface of zeolite micropores forms a surface-passivating layer around the zeolite nanoparticles that prevents their further aggregation (Serrano et al., 2009; Serrano et al., 2006). Nevertheless, TEM analysis of the hierarchical nanozeolites that prepared by this method showed a wide-range of crystal size distribution (200-400 nm), which were made of aggregation of extremely small units of 10 nm. Samples with large particle size hardly considered as true nanozeolites (Vuong and Do, 2007).

Therefore, improved synthesis of hierarchical nanozeolites in the presence of organic solvent has been developed to control the catastrophic aggregation of the zeolite primary nanoparticles. The solvothermal method was carried out in both single and also in two phase methods using various hydrophilic and hydrophobic solvents such as formamide, toluene, and 1-butanol or mixture of both (Vuong and Do, 2009; Vuong et al., 2010). The particle size of the obtained MFI structured hierarchical zeolite however is not completely in the range of 100 nm scale. Their SEM images show severe aggregation of particles. Moreover, the use of the hazardous solvents such as formamide and toluene as synthesis medium are not environmentally benign. For this reason, there is a continuous need for the development of a safe, sustainable and efficient synthesis strategy for hierarchical nanozeolites with the defined nanosize and morphology as a promise for their flourishing application in the field of catalysis.

Microporous zeolites like ZMS-5 and Beta are undoubtedly the best known for their acidic property and extensively studied in many acid catalyzed reactions such as cracking, alkylation, isomerization etc. (Corma, 1989). Generally, conventional zeolites possess high acid site concentration and narrower pores in the structure and are capable of promoting higher degree of cracking in bio-oil upgrading. The higher effective residence time caused by abovementioned zeolite properties incites cracking of hydrocarbon chain and light gases formation (Peng et al., 2012). Additionally, the existing catalysts for HDO reaction are facing various problems such as less selective of desired product and rapid deactivation because of the coke formation. The catalysts with poor stability is critical as it may lead to low catalytic activity (Wang, 2013). Nevertheless, the application of hierarchical nanozeolites are very rare in HDO reaction.

Up-to-date, very limited research work has been done yet in employing hierarchical nanozeolites Beta and ZSM-5 in hydroprocessing of vegetable oil to achieve high selective of diesel range hydrocarbons through HDO route. In this study, addition of inexpensive transition metal and by enhancing the external surface area and porosity volume of support materials are desirable to explore, which have vital role in promoting the catalytic activity of HDO reaction. Furthermore, the nature of the hierarchical nanozeolites acid sites and their structural-functional relationship in HDO reaction are determined. The understanding of initial rates and reaction mechanism of the hydroprocessing process is also important and it can be challenging when using real vegetable oils as feedstock. Herein, model compounds triolein, oleic acid and octanoic acid are selected to interpret the complete reaction pathway of the HDO reaction. This study is an effort to improve the quality and safety of environment and human life as it aims to develop a new and perhaps better heterogeneous catalysts that impulse enhanced catalytic reaction in biofuel industry.

1.3 Research Hypothesis

Two types of zeolites Beta and ZSM-5 in nanometer range are successfully synthesized under hydrothermal condition by modifying the zeolite synthesis parameters. Reducing the concentration of water and template in the starting gel and prolonging the aging time for the nucleation of zeolitic species have a pronounced effect in controlling the crystal size growth. Enhanced silylated nanozeolites with high external surface area, narrow particle size distribution and appropriate mesopores are prepared via solvothermal method using low hazard organic solvent as a medium for the surface silinization process and crystallization. The impregnation of reduced nickel onto the hierarchical nanozeolites is anticipated to improve the activity of HDO because of the synergistic effect between the dispersed active metal sites and the acidic nature of the supports. The hierarchical nanozeolite Beta and ZSM-5 possess both micro-mesoporosity and essential acid sites significantly improve the selectivity of the diesel range hydrocarbon over HDO route rather than DCN and/or DCO. Most importantly, it is predicted that the hierarchical catalysts are more stable and can be recycled several times compared to the conventional microporous zeolites. Finally, the nature of the nanozeolites acid sites and their structural-functional relationship as well as their kinetics and reaction mechanism in HDO reaction are established.

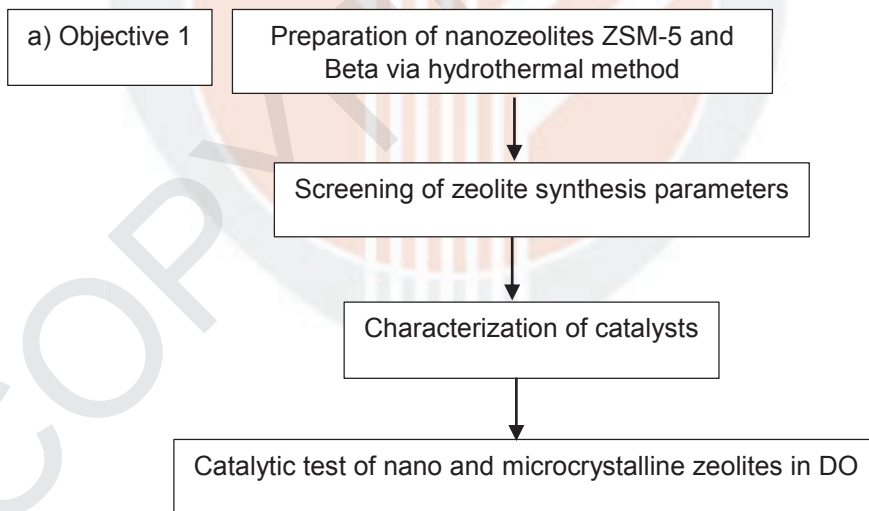
1.4 Research Objectives

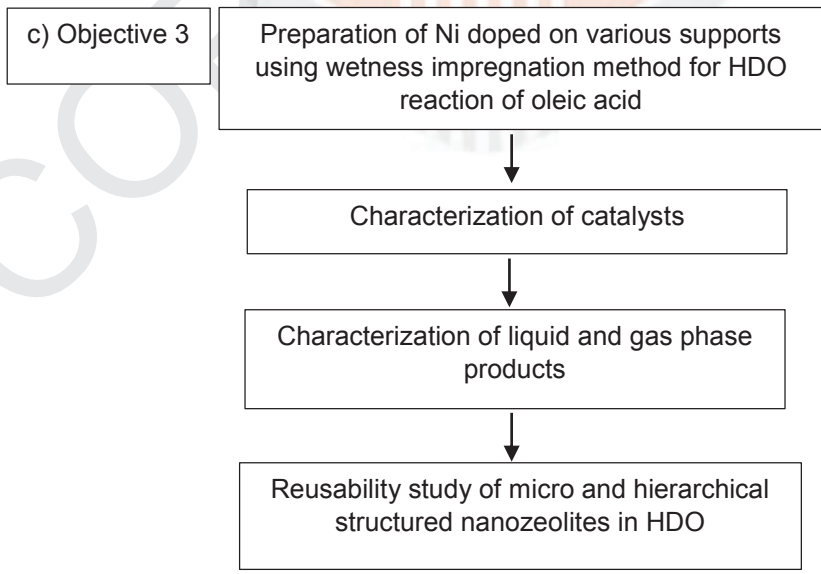
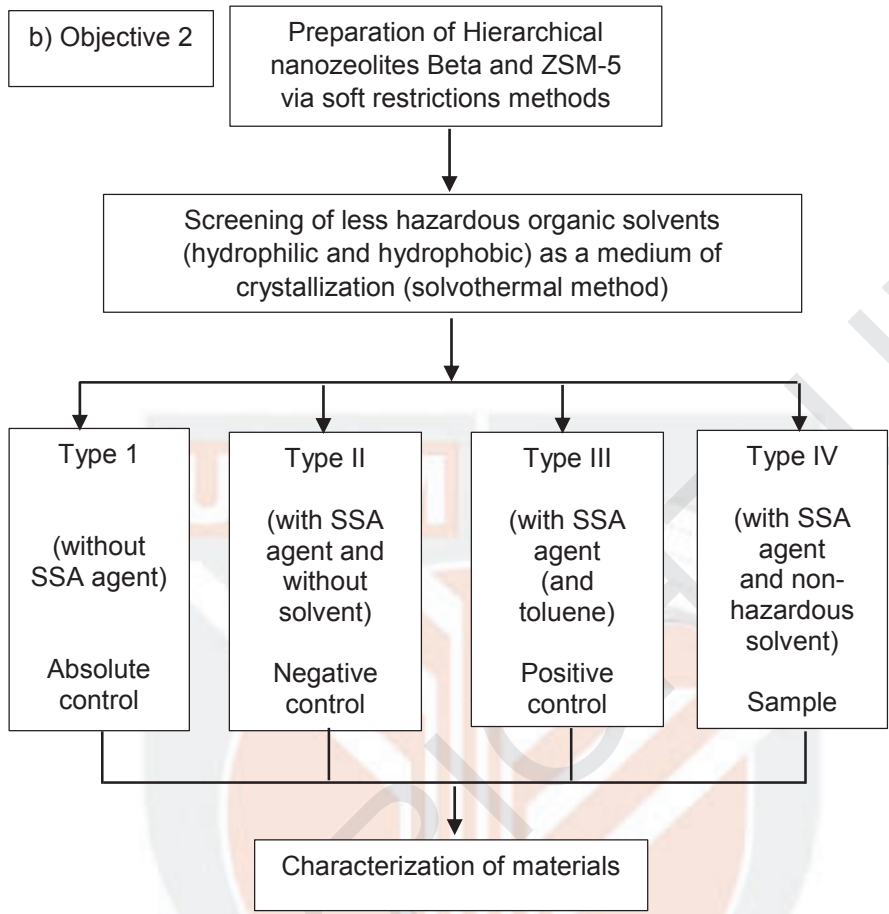
The main objectives of this research is to develop a new synthesis method for hierarchical nanozeolites and characterize them accordingly, as well as to evaluate their ability as alternative supports for HDO reaction. The aim of this study embarks on four different sections:

1. To prepare and characterize nanozeolites Beta and ZSM-5 with different synthesis parameters (including synthesis gel composition and crystallization condition); and test for DO reaction.
2. To prepare and characterize hierarchical nanozeolites Beta and ZSM-5 using various low hazard organic solvents as a medium for crystallization.
3. To evaluate the effect of Ni metal incorporation on various supports for enhancement in catalytic activity of oleic acid HDO reaction.
4. To investigate the initial rate and reaction mechanism of HDO of octanoic acid over Ni supported on nanozeolites, hierarchical nanozeolites and conventional zeolites.

1.5 Research Outline

Figure 1.1 (a-d) shows a detailed research design of this study, which was divided in four different stages with the aim to accomplish each individual research objectives as mentioned above. The objective one till four were discussed in chapter four till seven, respectively.





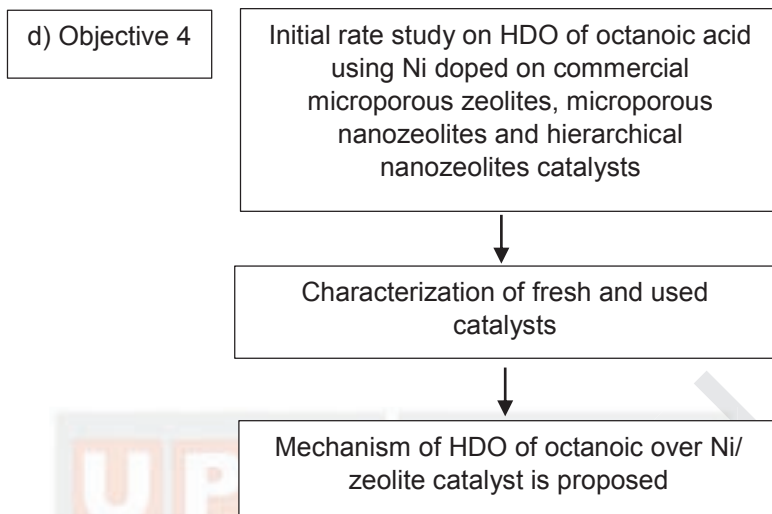


Figure 1.1: (a-d) Overall research workflow for all the objectives

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LIST OF PUBLICATIONS

Journal

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Mahashanon Arumugam, Taufiq-Yap Yun Hin and Sugeng Triwahyono. Hierarchical Nanozeolites ZSM-5 with Enhanced Textural Properties and Catalytic properties prepared by Surface Silanization Method- A Green Solvothermal Approach, International Conference on Catalysis 2018, Bangi-Putrajaya Hotel, Malaysia, 13th-15th November 2018.

Mahashanon Arumugam, Taufiq-Yap Yun Hin and Nurul Asikin-Mijan, Influence of the Synthesis Conditions – Generation of Nanocrystalline Zeolite Beta Catalyst for Production of Green Diesel, APCAT-7, Hotel The Lalit Mumbai, Maharashtra, Mumbai, 17th-21st January 2017.

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