# SYNTHESIS OF MESOPOROUS SODALITE USING VARIOUS ORGANIC TEMPLATES AS CATALYST IN KNOEVENAGEL CONDENSATION REACTION OF 2-NITROBENZALDEHYDE AND ETHYL ACETOACETATE

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“To my beloved parents for their unflagging love and support throughout my life and never failed to give me financial and moral support”

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All praises and thanks be to Allah for my life through all tests in the past four years. You have made my life more bountiful. May your name be exalted, honored, and glorified.

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# ABSTRACT

Sodalite is a type of zeolite having ultramicropore size and high thermal stability with strong basic property. However, microporous sodalite has several drawbacks in the catalyst application due to its small pore size (2.8 Å) and low surface area. To overcome these disadvantages microporous sodalite was modified to have mesoporous structure, while still maintaining its active sites suitable for catalyst applications. In this study, mesoporous sodalite was synthesized using various organic templates as structure directing molecules and used as a base catalyst in the Knoevenagel condensation reaction. A hierarchical mesoporous sodalite has been synthesized hydrothermally at 150ºC for crystallization using various mesotemplates. Results from XRD and FTIR spectroscopy showed that all templates being used in the synthesis produced sodalite phase. The sodalite synthesized using organosilane template and a dual template containing a mixture of tetrapropylammonium hydroxide and cetyltrimethylammonium bromide, have shown mesoporosity, as proven by nitrogen adsorption analysis. The field emission scanning electron microscopy (FESEM) micrographs of the mesoporous sodalite obtained showed spherical morphology in the size range ~ 10-16 nm. $^{29}$Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy showed the sodalite framework has a Si/Al ratio equal to 1, while $^{27}$Al MAS NMR spectrum exhibited the unsymmetrical tetrahedral Al. The synthesized sodalite samples which were modified with metal ions ($K^+$, $Cs^+$) enhanced the sodalite basicity. Results from Hammet indicators and temperature programmed desorption of $CO_2$ studies revealed that potassium mesoporous sodalite prepared using dual template has the highest strength and amount of basic sites. The reactivity for all of the prepared sodalite samples was evaluated in the Knoevenagel condensation of 2-nitrobenzaldehyde and ethyl acetoacetate, producing 4-(2-nitrophenyl)-but-3-en-2-one as the main product, and *trans*-2-nitrocinnamic acid as the side product. All synthesized mesoporous sodalites were more reactive than the microporous sodalites counterpart, producing > 70% selectivity for the main product. Based on the conversion of reactant, the potassium mesoporous sodalite using dual template has shown the most active catalyst which gave 95% conversion at 150$^{o}$C and 6 hours reaction using 0.2 g catalyst. Result from the experimental study was in accordance with the response surface methodology (RSM) findings for the optimum reaction parameters which were at 150$^{o}$C, 6 hours reaction time, 0.2 g catalyst for 97.1% conversion. This study has proven that besides basicity, hierarchical mesoporosity of sodalite is important for the enhancement of the reactivity of the sodalite catalyst for reactions involving larger molecules such as in the Knoevenagel reaction.

# ABSTRAK

Sodalit adalah sejenis zeolit yang mempunyai saiz ultramikroliang dan kestabilan haba yang tinggi dengan sifat bes yang kuat. Walau bagaimanapun, sodalit mikroliang mempunyai beberapa kelemahan dalam penggunaannya sebagai mangkin kerana saiz liang kecil (2.8 Å) dan luas permukaan yang rendah. Untuk mengatasi kelemahan ini sodalit mikroliang telah diubahsuai untuk mempunyai struktur mesoliang, di samping masih mengekalkan tapak aktif yang sesuai untuk aplikasi sebagai mangkin. Dalam kajian ini, sodalit mesoliang telah disintesis menggunakan pelbagai templat organik sebagai molekul pengarahan struktur dan digunakan sebagai mangkin bes dalam tindak balas kondensasi Knoevenagel. Sodalit mesoliang berhierarki telah disintesis secara hidroterma pada 150°C untuk penghabluran menggunakan pelbagai jenis mesotemplat. Keputusan XRD dan spektroskopi FTIR menunjukkan bahawa semua templat yang digunakan dalam sintesis menghasilkan fasa sodalit. Sodalit yang disintesis menggunakan templat organosilana dan dwi templat yang terdiri daripada campuran tetrapropilammonium hidroksida dan setiltrimetilammonium bromida, telah menunjukkan sifat mesoliang, seperti yang dibuktikan oleh analisis penjerapan nitrogen. Mikrograf dari mikroskopi elektron pengimbasan pancaran medan (FESEM) bagi sodalit mesoliang yang diperoleh menunjukkan morfologi sfera dalam julat saiz ~ 10-16 nm. Spektroskopi $^{29}$Si putaran sudut ajaib-resonans magnet nukleus (MAS NMR) menunjukkan bingkaian sodalit mempunyai nisbah Si/Al bersamaan dengan 1, sementara spektrum $^{27}$Al NMR MAS mempamerkan Al tetrahedron tak simetri. Sampel sodalit yang disintesis, diubah suai dengan ion logam ($K^+$, $Cs^+$) untuk meningkatkan sifat bes sodalit. Keputusan daripada kajian penunjuk Hammet dan suhu penyahjerapan terprogram CO2 menunjukkan kalium sodalit mesoliang yang menggunakan dwi templat mempunyai kekuatan dan jumlah tapak bes tertinggi. Kereaktifan semua sodalit yang disediakan telah dinilai dalam kondensasi Knoevenagel antara 2-nitrobenzaldehid dan etil asetoasetat, menghasilkan 4-(2-nitrofenil)-but-3-en-2-on sebagai hasil utama dan *trans* asid 2-nitrosinamik sebagai hasil sampingan. Semua sodalit mesoliang yang disintesis adalah lebih reaktif berbanding dengan sodalit mikroliang, menghasilkan > 70% kepilihan untuk hasil utama. Berdasarkan pertukaran bahan tindak balas, kalium sodalit mesoliang menggunakan dwi templat telah menunjukkan mangkin yang paling aktif yang memberikan 95% penukaran pada suhu 150°C dan 6 jam tindak balas, menggunakan 0.2 g mangkin. Keputusan daripada kajian eksperimen adalah selaras dengan kaedah permukaan respons (RSM) untuk parameter tindak balas optimum iaitu suhu 150°C, 6 jam masa tindak balas, 0.2 g mangkin bagi 97.1% penukaran. Kajian ini telah membuktikan bahawa di samping sifat bes, sodalit bermesoliang hierarki adalah penting untuk peningkatan kereaktifan pemangkin sodalit bagi tindak balas yang melibatkan molekul yang lebih besar seperti dalam tindak balas Knoevenagel.

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| | | |
|---|---|---|
| BET | - | Brunauer–Emmett–Teller |
| EDX | - | Energy Dispersive X-Ray Spectroscopy |
| FESEM | - | Field Emission Scanning Electron Microscopy |
| FTIR | - | Fourier Transform Infrared |
| GC-FID | - | Gas Chromatography-Flame |
| GC-MSD | - | Gas Chromatography-Mass Spectroscopy Detector |
| NMR | - | Nuclear Magnetic Resonance Spectroscopy |
| RSM | - | Response Surface Methodology |
| SDA | - | Structure Directing Agents |
| TPD-$CO_2$ | - | Temperature Programmed Desorption of $CO_2$ |
| XRD | - | X-Ray Diffraction Spectroscopy |
| NaMPSOD | - | Sample synthesized without template and using fumed silica as silica source |
| KMPSOD | - | Sample synthesized without template and using fumed silica as silica source ion exchanging with $K^+$ |
| CsMPSOD | - | Sample synthesized without template and using fumed silica as silica source ion exchanging with $Cs^+$ |
| NaMPSOD-OS | - | Sample synthesized using organosilane as template and fumed silica as silica source |
| KMPSOD-OS | - | Sample synthesized using organosilane as template and fumed silica as silica source ion exchanging with $K^+$ |
| CsMPSOD-OS | - | Sample synthesized using organosilane as template and fumed silica as silica source ion exchanging with $Cs^+$ |
| NaMPSOD-TC | - | Sample synthesized using mixture of TPA&CTABr as templates and fumed silica as silica source |

| | | |
|---|---|---|
| KMPSOD-TC | - | Sample synthesized using mixture of TPA&CTABr as templates and fumed silica as silica source ion exchanging with $K^+$ |
| CsMPSOD-TC | - | Sample synthesized using mixture of TPA&CTABr as templates and fumed silica as silica source ion exchanging with $Cs^+$ |
| NaMPSOD-CT | - | Sample synthesized using CTABr as template and fumed silica as silica source |
| NaMPSOD-DD | - | Sample synthesized using DDAB as template and fumed silica as silica source |
| NaMPSOD-P | - | Sample synthesized using PEG-PPG-PEG as template and fumed silica as silica source |
| NaMPSOD-PV | - | Sample synthesized using PVB as template and fumed silica as silica source |
| NaMPSOD-TE | - | Sample synthesized using TEA as template and fumed silica as silica source |
| TPA | - | Tetrapropylammonium hydroxide |
| CTABr | - | Cetyltrimethylammonium bromide |
| DDAB | - | Dimethyldioctadecylammonium bromide |
| PEG-PPG-PEG | - | Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) |
| PVB | - | Polyvinyl butyral |
| TEA | - | Tetraethylammonium hydroxide |
| RHA | - | Rice husk ash |
| TEOS- | - | Tetraethyl orthosilicate |
| $H_0$ | - | Acidity function |
| 3DOM-I | - | Three-dimensionally ordered mesoporous-imprinted |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of the Study

Zeolites are microporous (1-20 Å diameters) crystalline solids with well-defined structures. Zeolites are crystalline, hydrated aluminosilicates with open three-dimensional framework structure built of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedral linked by sharing of an oxygen atom, to form regular intracrystalline cavities and channels of molecular dimensions. The framework structure may contain linked cages, cavities or channels withthe size which allows the small molecules to enter the limiting pore sizes. The pore sizes are roughly between 3 and 10 Å in diameter. Zeolites are crystalline hydrated aluminosilicates of alkaline and earth-alkaline elements (particularly of sodium and calcium, compositionally similar to clay minerals, but differing in their well-defined three-dimensional neon- and micro-porous structure. Aluminum, silicon, and oxygen are arranged in a regular structure of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral units that form a framework with small pores (also called tunnels, channels, or cavities) of about 0.1-2 nm diameter running through the material. Because of their unique porous properties, zeolites are used in a variety of applications. Zeolites have been used as ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are also often referred to molecular sieves. Zeolites are porous, hydrated aluminosilicates. They may be natural minerals or synthetic materials. The general chemical composition of a zeolite is:

$$M_{x/n}\,[(AlO_2)_x\,(SiO_2)_y].\,wH_2O$$

where M is an alkali or alkaline earth cation, n is the valence of the cation, w is the number of water molecules per unit cell, x and y are the total number of tetrahedral per unit cell, and the ratio y/x usually has values of 1 to 5, though for the silica zeolite y/x can be ranging from 10 to 100 [1].

There are five characteristics of zeolites. The first characteristic is tectosilicates, which three dimensional structure is built from tetrahedra of Si and Al. However,some of the silicon atoms have been replaced by aluminum, (i.e. the (Si+Al)/O = ½), which usually denotes the T-atoms. The second characteristic isopen framework structure, which is built from $TO_4$-tetrahedra, consisting pores and voids with the periodic manner (i.e. crystalline materials). The third characteristic is counter ions (cations) which are presented in order to compensate for the negative framework charge that is created by aluminum substitution. The counter ions are situated and mobile in the pores and voids. The four characteristic of zeolite is that the voids and pores are filled through the water molecules (present zeolitic water). One measure of the porosity is the amount of adsorbed water which is presented in the pores and voids, and may remove by the heating and readsorbed at lower temperatures. The fifth characteristic of zeolites refers to Loewensteins rule, which imposes a limit amount of aluminum, may be substituted into the framework.There is no Al-O-Al presented in the tectosilicates. It means, only half of the silicon atoms may be substituted by aluminum which indicates the Si/Al ratio is 1.

Zeolites have the ability to act as catalyst for chemical reactions which takes place within the internal cavities. An important class of reactions is that catalyzed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This has been exploited in many organic reactions, including crude oil cracking, isomerization and fuel synthesis. Microporous crystalline aluminosilicate zeolites are widely used in petrochemical and fine-chemical industry because of their large surface area, high adsorption capacity, high thermal and hydrothermal stabilities, strong acid sites within their defined micropores, and shape selectivity in catalysis. According to Zaarour *et al.* [2], zeolites with uniform pore size, adjustable acidity, and good stability have been regarded as one of the most important catalysts in petrochemical industry due to their excellent catalytic performance. Zeolite can also serve as oxidation or reduction catalysts.

However, zeolite with sole micropores are imposed by severe mass-transfer constrains, which results in poor catalytic performance (such as life time and convention in bulky substrate catalytic reaction. The relatively small pore size of the microporous zeolites (pore diameter < 1.5 nm) restricts their further applications because of slow diffusion of reactants and products from the active sites of the zeolites [3].

In many catalytic applications, the main drawback of zeolites is their intricate pore and channel systems in the molecular size ranging from 0.3 to 1.5 nm. It makes large molecules cannot react effectively over these microporous materials because of the limitation of their small pore sizes. To solve the diffusion problems of guest species in zeolites, mesoporous aluminosilicate materials with adjustable larger pore sizes, such as MCM-41 and SBA-15 have been successively invented [4]. These materials can overcome the pore size constraint of microporous zeolites and allow the diffusion of larger molecules. However, as compared with conventional zeolites, these mesoporous materials exhibited insufficient hydrothermal stability and acidity, which limits their use as catalysts in a wide range of industrial processes and reactions.

Several different methods have been proposed to overcome the drawback of these limitations of microporous zeolites. To overcome these problems, many efforts have been devoted to synthesize nanosized zeolite, ultralarge pore zeolites, and hierarchical mesoporous zeolite. These approaches consist of synthesizing ordered mesoporous materials with ordered pore (2-50 nm).The exploitation of template in mesoporous zeolites has clearly been receiving a great deal of attention for those working in zeolite synthesis. Since mesopore-modified zeolites have shown promising properties (activity and selectivity) in catalytic processes, the next portion of this contribution deals with the hottest current topics and important progress in this field.

Up to date zeolites with mesoporosity have been successfully synthesized such as ZSM-5 [4], zeolite Y [5], zeolite A [6] and zeolite X [7]. It pave a way to introduce mesoporous into the zeolite crystals in recent years, and thus have the advantages of both meso structured materials (fast diffusion and accessible for bulky molecules) and microporous zeolite crystals (strong acidity and high hydrothermal stability). Mesoporous ZSM-5 and A zeolites were synthesized using an amphiphilcorganosilicate as mesopore-directing agent [8]. Later mesoporous ZSM-5 zeolite was also prepared using a silylatedpolyethylenimine as mesopore-directing agent. Following these attempts, mesoporous zeolites have been widely investigated and the most used templates are polymers, long chain organosilicates, and amphiphilc surfactants. For example, mesoporous ZSM-11 templated by polyvinyl butyral, mesoporous Y templated by long chain organosilicates [9] and mesoporous ZSM-5 templated by CTAB or F127 or P123 have been reported [10]. Hwang *et al.* [11] designed a kind of bifunctional surfactants, such as $C_{22}H_{45}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_6H_{13}(C_{22–6–6})$ and $C_{18}H_{37}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_{18}H_{37}(C_{18–6–6–18})$, which can direct the formation of zeolite structures on the mesoporous and microporous length scales simultaneously, yielding ZSM-5 zeolite nanosheets with a thickness (2 nm) of only a single unit cell or ordered mesoporous zeolites with hexagonal mesophase and MFI-like zeolite framework, respectively. Qin *et al*. [6] described that a novel synthetic route was designed, employing both high temperature and a nontoxic organic structure-directing agent (SDA), for the synthesis of high silica zeolite Y. The *N*-methylpyridinium is used as an organic SDA that is stable during the synthesis, and the high silica zeolite Y shows high hydrothermal stability and good catalytic performance, as well as excellent adsorptive properties.

Zeolite nanocrystals from three-dimensionally ordered mesoporous-imprinted (3DOm-i) silicalite-1 prepared by a fragmentation method involving sonication and dissolution within a certain pH range. 3DOm-i silicalite-1 with spherical elements with diameters ranging from 10 to 40 nm and a wide range of crystal sizes (100-200 nm, 500-600 nm, and 1-2 μm) were used as the starting material [12].

According to Saada *et al.*[13], BEA (Beta polymorph A), LTA (Linde Type A, zeolite A), FAU (Faujasite) and LTL (Linde Type L, zeolite L) with ordered mesoporosity have been synthesized within the confined space of 3DOm carbon by conventional hydrothermal treatment. They can be easily tuned by varying the mesopore size of carbon and mesoporous structure of the carbon template.A wide range of crystal morphologies can be achieved by varying the nucleation and crystal growth rate.

Wang *et al.* [14] synthesized a mesoporous zeolite beta using mesoscale cationic polymers as soft template, which was used as catalyst in alkylation of benzene with 2-propanol.Mesoporous beta sample exhibited much higher activity and isopropylbenzene selectivity (both close to 100%) than the conventional beta, and more importantly, remarkably slow deactivation over the mesoporous sample could be also observed.

Sodalite is kind of zeolite with ultramicropore size, high aluminum content (Si/Al = 1), and high stability in basic solution. Sodalite is an ultramicropore zeolite, which aluminosilicate framework consists of a 4-membered ring aperture with a pore size of 2.8 Å, known to be the smallest pore size in zeolite family. Because of its small pore size and high ion exchange capacity, sodalite has been considered as a good candidate material for a wide range of applications such as hydrogen storage, optical materials and hydrogen separation but one disadvantage of sodalite is the pore sizes which are too small to allow access to bulky organic molecules therefore mesoporous sodalite, with a surface area of around 190 $m^2/g$, has been synthesized and used as a catalyst for base-catalyzed reactions and a catalyst support of palladium metal particles for crosscoupling reactions [15]. Figure 1.1 shows the structure of sodalite.

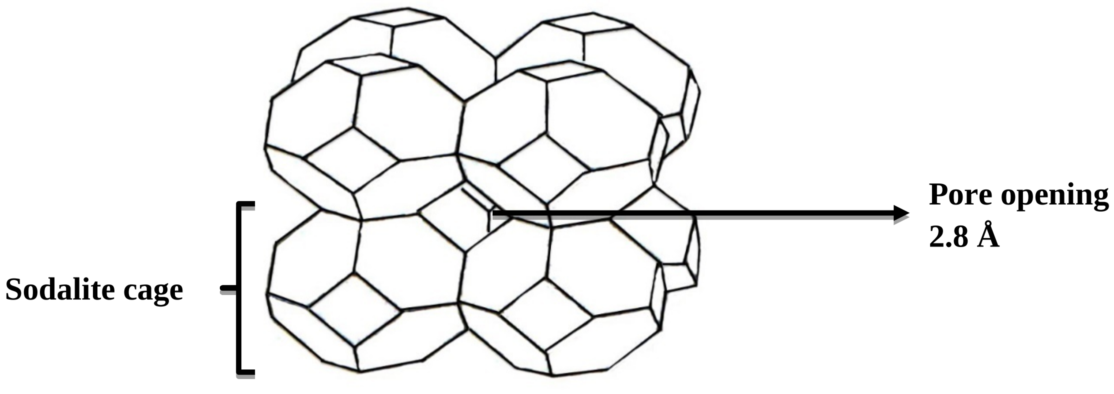

**Figure 1.1:** Sodalite framework [16]

Knoevenagel condensation is a classic C-C bond formation reaction in organic chemistry field. These condensations occur between aldehydes or ketones and active methylene compounds with ammonia or another amine as a basic catalyst in an organic solvent. Knoevenagel reaction carries out at the presence of sodalite with mesoporosity as a base catalyst. It causes to produce product that is useful for green chemistry, in the pharmaceutical, and in the line of calcium channel blockers. It works by blocking voltage-gated calcium channels in cardiac muscle and blood [15].

According to Shanbhag *et al.*[15], Knoevenagel condensation of 4-isopropylbenzaldehyde (4-IPB) with ethyl cyanoacetate (ECA) is catalyzed by mild basic catalysts. The activity of KMPSOD (mesoporous sodalite modified with $K^+$) was compared with that of KAlMCM-41 (AlMCM-41 modified with $K^+$) and CsNaX(NaX modified with $Cs^+$) which contained similar Si/Al ratios but differed in pore size, pore structure, and basicity. KMPSOD was the most active catalyst (78%) followed by MPSOD (mesoporous sodalite) (70%), KAlMCM-41 (46%), and CsNaX (35%) after 1 h reaction. The higher activity of KMPSOD was attributed to the basic sites located in their mesopores, which facilitated the diffusion of bulky molecules. It showed the possibility of modifying the ultramicropore zeolite such as sodalite to having high specific surface area and mesoporosity [16].

## 1.2 Statement of the Problem

Zeolites are microporous crystalline aluminosilicate with open three dimensional framework structures. Because of their unique porous properties, they are used in various reactions. Zeolites have the ability act as catalyst for chemical reactions.The relatively small pore size of the microporous zeolite (pore diameter less than 2 nm), restricts their applications because of slow mass transfer of bulky reactants and products from the active sites of the zeolite.

Sodalite is kind of zeolite with ultramicropore size, high aluminum content (Si/Al = 1), and high stability in basic solution. In general, the composition of sodalite is $M_8 [T_{12}O_{24}] X_2$, where X is a monovalent guest anion such as chloride in the mineral sodalite, M is an alkali or alkaline earth cationandT is Si and Al. Because of its small pore size and high ion exchange capacity, sodalite has been considered as a good candidate material for a wide range of applications such as hydrogen storage, optical materials and hydrogen separation, but one disadvantage of sodalite is the pore sizes which are too small to allow access to bulky organic molecules. Thus it has not found any significant catalytic application due to its inaccessibility cages with small pore openings. The slow diffusion of sodalite which refers to the intracrystalline diffusion is the most problematic issue for using sodalite as a heterogeneous base catalyst in various reactions [17]. In order to solve this problem, the pore size must increase in the mesoporous rangewith ordered pore (2-50 nm) and make particle size in the nano size range with the decrease path length to prepare sodalite with improving the accessibility to the active sites.In fact,having mesoporosity lead to more active sitesthat can be reached by the reactants. The active sites which are located inside mesopores and the large external surface area of mesoporous sodalite, exhibit much higher effectiveness factors for the reaction involving bulky molecules. Therefore, it is a challenge to modify the microporous sodalite to mesoporous sodalite with special properties including high aluminum content, highly mesoporous crystalline zeolitic walls, and high surface area that facilitated the diffusion of bulky molecules.

Shanbhag *et al.* [15] reported the mesoporous sodalite synthesized using amphiliphic organosilane surfactant as structure directing molecule. The long chain length of this surfactant has great effect on micelle size, pore volume and mesoporosity. It is shown possibility of modifying the ultramicropore zeolite, such as sodalite to mesoporous sodalite. Since the synthesized mesoporous sodalite has highly aluminum content, so the active basic sites of mesoporous sodalite are strong enough to catalyze the reaction, and it leads to high conversion of reactants to products. Previous study has shown that sodalite with micropore has special basic sites which equivalent to that of basic metal oxides when tested on Knoevenagel reaction [15]. As such, the study of the basicity of the obtained mesoporous sodalite in Knoevenagel might give different result from that of microporous sodalite. According to Shanbhag *et al.* [15], mesoporous sodalite with a mesoporous/microporous hierarchical structure was successfully synthesized using an organosilane surfactant. It showed about 10-fold high surface area and 4-fold large pore volume, as compared with sodalite with solely microporous structure. The basicity of mesoporous sodalite was higher than that of microporous sodalite. The catalytic activities of this mesoporous sodalite were tested for various base catalyzed reactions involving bulky and small substrates. The catalyst showed higher activity and longer lifetime than microporous sodalite.

Since 2012, there has been no reported on other types of structure directing molecule beside amphiliphic organosilane in the formation of the mesoporous sodalite. Thus, this research focuses on finding the other types of structure directing agents as organic templates (organosilane (trimethoxsilylpropyldimethyloctadecylammonium chloride) and mixture of tetrapropylammonium hydroxide (TPA) with cetyltrimethylammonium bromide (CTABr) with mole ratio of 1:1), which can interact strongly with silicate solution and can be used to form mesoporous sodalite.

## 1.3 Objectives of the Study

1. To synthesize mesoporous sodalite using different structure directing organic templates and characterize the physical and chemical properties of mesoporous sodalite.

2. To modify the basicity of mesoporous sodalite by ion-exchanging with different alkali metals.

3. To study the strength and amount of basic sites of mesoporous sodalite.

4. To evaluate the activity of mesoporous sodalite as a catalyst in Knoevenagel reaction and compare with microporous sodalite.

## 1.4 Scope of the Study

The scope of this study included hydrothermal synthesize of mesoporous sodalite as a catalyst. Sodium aluminate was used as Al source, while fumed silica, was used as silica source and $Na^+$ as a counter ion. Different templates were used for synthesis of mesoporous sodalite include organosilane (trimethoxsilylpropyldimethyloctadecylammoniumchloride),dimethyldioctadecylammonium bromide (DDAB), cetyltrimethylammonium bromide (CTABr), tetreaethylammonium hydroxide (TEA), polyvinyl butyral (PVB), poly(ethyleneglycol)-block-poly(propyleneglycol)-block-poly(ethyleneglycol) (PEG-PPG-PEG),and mixture of tetrapropylammonium hydroxide (TPA) with cetyltrimethylammonium bromide (CTABr) with mole ratio of 1:1.

X-ray diffraction (XRD) patterns were recorded with a Rigaku Multiflex Diffractometer equipped with Cu K$\alpha$ radiation (40 kV, 40 mA). The presence of tetrahedral $TO_4$ (T = Si or Al) bonding and formation of zeolite were determined using Fourier transform infrared spectroscopy (FTIR). The spectrum was elucidated for zeolite framework structure at wavenumbers between 400-1500 $cm^{-1}$. The textural properties of the samples were measured by $N_2$ sorption at liquid nitrogen temperature by Micromeritics 2010 v3.01g volumetric adsorption analyzer. Samples were dried at 300°C in a dynamic vacuum for 2 h before the $N_2$physisorption measurements. The specific surface area was determined using the standard BET method on the basis of adsorption data. The pore size distributions were calculated from both the adsorption and desorption branches of the isotherms using the BJH method and the Kelvin equation. Morphology and elements in the sample were observed by FESEM equipped with energy dispersion X-ray spectrometer (FESEM-EDX, JEOL JSM-6710F). After the morphology was observed on the FESEM, the composition of the element in specific area was determined by using EDX. The EDX was determined by using FESEM equipped with energy dispersion X-ray spectrometer (FESEM-EDX, JEOL JSM-6710F). $^{29}Si$ and $^{27}Al$ nuclear magnetic resonance MAS NMR was carried out by using Bruker Advance 400 with 4 mm zirconia motor 79.47 MHz and 104.23 MHz for $^{29}Si$ and $^{27}Al$ MAS NMR respectively to determine the local environment of tetrahedral $SiO_4$ and tetrahedral

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