SYNTHESIS OF MESOPOROUS SODALITE BY MIXED QUATERNARY AMMONIUM CATION TEMPLATES FOR KNOEVENAGEL CONDENSATION REACTION

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"I dedicate this entire work to my beloved family members and also to all my friends. Thanks for keep supporting me"

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ABSTRACT

Sodalite (SOD) is a microporous zeolite having ultra-fine size of pore about 2.8 Å. This property limits its role as a catalyst for the reaction involving bulky molecules. To overcome this disadvantage, suitable mesotemplate can be added to create mesoporosity in microporous SOD. This study focused on the synthesis of SOD having mesoporosity using dual templates approach. A series of SOD were synthesized by mixing tetrapropylammonium (TPA) with different quaternary ammonium cations. As comparison, microporous SOD (Na-SOD) has also been synthesized without the presence of templates. The resulting SOD samples were characterized using XRD, FTIR and N_2 adsorption-desorption measurement. The successful formation of SOD crystal phase for all SOD samples was confirmed from XRD patterns and supported by FTIR results that showed all SOD samples have the characteristic of SOD framework. However, N_2 adsorption-desorption results confirmed that only SOD sample prepared by mixing TPA with organosilane (SOD-TO) showed the characteristic of mesoporosity with a narrow pore distribution peak centered at *ca.* 66 Å. For basicity study, Hammett indicator test showed that the strength of the basicity of all SOD samples was estimated in the range: $8.2 \leq pKa \leq 18.4$. The results from back titration method found that the SOD-TO sample possessed the highest average amount of basicity as compared with other SOD samples. The comparison of the strength and the amount of basicity for microporous SOD, Na-SOD and mesoporous SOD, SOD-TO samples were measured using TPD-CO_2 analysis. The results showed that the SOD-TO sample has higher strength and amount of basic sites than the Na-SOD sample at temperature below 500°C. The catalytic testing of all SOD samples in the Knoevenagel condensation reaction of benzaldehyde and diethyl malonate was carried out giving diethyl-2-benzylidenemalonate as a main product. Results showed that all SOD catalyst were active for the Knoevenagel condensation reaction. From the result of catalyst testing, the basicity and surface area does give an impact during the reaction. The SOD-TO catalyst possessing the highest amount of basicity and the highest surface area with mesoporosity in its structure gave the highest percentage of conversion which was 96.29%.

ABSTRAK

Sodalit (SOD) ialah zeolit mikroliang yang mempunyai liang bersaiz sangat halus iaitu sekitar 2.8 Å. Ciri ini menghadkan peranan SOD sebagai mangkin bagi tindak balas yang melibatkan molekul-molekul yang besar. Untuk mengatasi kekangan ini, mesotemplat yang sesuai boleh ditambahkan bagi menghasilkan mesoliang dalam SOD mikroliang. Kajian ini memberi fokus dalam mensintesis SOD yang mempunyai mesoliang menggunakan pendekatan dwi templat. Satu siri SOD telah disintesis dengan campuran tetrapropilamonium (TPA) dengan kation amonium kuaterner yang berbagai. Sebagai perbandingan, SOD mikroliang (Na-SOD) juga telah disintesis tanpa kehadiran templat. Sampel SOD yang terhasil telah dicirikan menggunakan XRD, FTIR dan penjerapan gas Nitrogen (N_2). Corak XRD telah mengesahkan pembentukan fasa kristal SOD untuk semua sampel SOD dan telah disokong dengan keputusan FTIR yang menunjukkan semua sampel SOD mempunyai ciri-ciri kerangka SOD. Walau bagaimanapun, keputusan penjerapan gas N_2 telah mengesahkan hanya sampel SOD yang disintesis hasil campuran TPA dengan organosilana (SOD-TO) menunjukkan ciri-ciri mesoliang dengan puncak penyebaran liang berpusat di *ca.* 66 Å. Untuk kajian kebesan, ujian penunjuk Hammet menunjukkan kekuatan kebesan semua sampel SOD dianggarkan dalam lingkungan: $8.2 \leq pKa \leq 18.4$. Hasil daripada kaedah titratan berbalik mendapati sampel SOD-TO mempunyai amaun purata kebesan paling tinggi berbanding dengan sampel SOD yang lain. Perbandingan untuk kekuatan dan jumlah kebesan untuk SOD mikroliang (Na-SOD) dan SOD mesoliang (SOD-TO) telah dijalankan menggunakan analisis TPD-CO_2. Keputusan mendapati sampel SOD-TO mempunyai kekuatan dan jumlah kebesan yang lebih tinggi berbanding sampel Na-SOD pada suhu di bawah 500°C. Ujian mangkin untuk semua sampel SOD dalam tindak balas kondensasi Knoevenagel antara benzaldehid dan dietil malonat telah dijalankan untuk menghasilkan dietil-2-benzilidenemalonat sebagai hasil utama. Keputusan menunjukkan semua mangkin SOD adalah aktif untuk tindak balas kondensasi Knoevenagel. Hasil daripada ujian mangkin, kebesan dan luas permukaan kawasan memberi impak semasa tindak balas. Mangkin SOD-TO yang mempunyai amaun kebesan dan luas permukaan yang paling tinggi dengan kehadiran mesoliang dalam strukturnya memberikan peratusan penukaran yang paling tinggi iaitu 96.29%.

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ABBREVIATIONS

SOD/s	-	Sodalite/s
ZSM	-	Zeolite Socony Mobil
LTA	-	Linde Type A
FAU	-	Faujasite
nm	-	nanometer
MCM	-	Mobile Crystalline Material
SDA/s	-	Structure directing agent/s
XRD	-	X-ray diffraction
Cu-Kα	-	X-ray diffraction from copper Kα energy levels
2θ	-	Bragg angle
FTIR	-	Fourier Transform Infrared
KBr	-	Potassium bromide

CHAPTER 1

INTRODUCTION

1.1   Background of Study

Zeolites are crystalline aluminosilicate solids made up of three dimensional (3D) framework structures of SiO_4 and AlO_4 tetrahedra. These tetrahedra are linked together by sharing all the oxygen atoms and formed a uniformly pores or channels of molecular dimensions. As a result, most of zeolites are acted as a sieve on a molecule scale which adsorbs only molecules that can fit inside the pores [1]. Besides, the aluminosilicate framework of zeolites carried a net of negative charged which later balanced by the positive cations. Some common cations that help to preserve the electroneutrality of the zeolites are elements from the IA and IIA groups of the periodic table. Those cations are able to cation exchanged and result in the narrowing of the pore diameter of the zeolite channels [2]. These properties play important roles to the uses of zeolite in many applications.

Zeolites are participated in a variety of applications due to their unique porous properties. Three most important areas of zeolites are catalysis, ion exchange and gas separation. In catalytic applications, zeolites are involved in wide range of catalytic reactions including acid-base and metal induced reactions. Some processes are hydrocracking of heavy petroleum distillates, the synthesis of ethylbenzene and the disproportionation of toluene. In ion exchange applications, synthetic zeolites with a maximum cation exchange capacity are of interest as ion exchangers and adsorbents. These zeolites are used as builders in laundry detergents that help to encapsulate other cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations in

exchange for sodium ions (Na^+) [3]. In gas separation areas, the contribution of synthetic zeolites is in pressure swing adsorption (PSA) technology for the production of oxygen from air. The capability of zeolites to adsorb polar compounds makes them often used in separation and purification of gases [4].

The versatility properties of zeolites mainly their microporous pores have brought significant uses in several industrial processes nowadays. However, in the catalytic reactions, the presence of micropores (< 2 nm) on the zeolites will limit its performance usually in the reaction that involving bulky molecules. The micropore structures lead to diffusion limitations that hinder larger or bulky sized reactant or product molecules from approach or leave the active site of zeolites [5]. Previous study has found that ZSM-5 zeolite fails to catalyze reaction with large molecules due to their diffusion restrictions in the micropore channels [6]. Therefore, in the last few years, researchers have conducted many studies in order to overcome the limitations faced by microporous zeolites. Many studies are focusing in creating a new structure of zeolite that has ability to enhance diffusion and accessibility for larger or bulky molecules.

One of the best strategies to overcome the limitation faced by microporous zeolites is by synthesizing a new zeolite that consists of micropores and mesopores (2-50 nm) in one material. This strategy leads to the formation of hierarchical porous zeolites or also known as mesoporous zeolites [7]. The formation of mesoporous zeolites will then enhance the approachability to the active site and thus improve the catalytic performance involving large or bulky molecules [8]. There are many approaches or methods to create the mesoporosity in the zeolite structure such as destructive strategies, dealumination or desilication post-synthetic procedures and the direct or "one-pot" synthesis method with the presence of hard or soft templates. Among them, the direct synthesis with the presence of templates allows reducing in the number of synthetic steps during the preparation of mesoporous zeolites. Thus, low cost method for synthesizing mesoporous zeolites is available. In addition, this approach leads to simultaneously formation of mesoporosity in zeolite structure [9].

Recently, soft templating approaches have great attention in the formation of mesoporous zeolites. Some examples of soft templates are surfactants and polymers [10]. An amphiphile organosilane is an example of amphiphilic surfactants that contained a quaternary ammonium site along with a trimethoxysilyl site. Both these sites are responsible for the interaction between the surfactant with the growing zeolite entities. In addition, a long hydrophobic tail presence in the amphiphile organosilane leads to the formation of mesostructure in the zeolite framework. Previous study successfully synthesized a microporous-mesoporous ZSM-12 zeolite with the presence of [3-(trimethoxy-silyl)propyl] octadecyldimethylammonium chloride (TPOAC) as a mesopores directing agent [11]. Cationic surfactants are another example of surfactants that contained quaternary ammonium sites in their structure. Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant that often used for the synthesis of ordered mesoporous zeolites [12]. Previous study has reported the preparation of mesoporous zeolite Y from an alkaline solution containing CTAB. The major advantage by using soft templates is these templates can be easily removed through a calcination process [13].

In spite of using only one soft template, the mesoporous zeolites can also be prepared through a direct synthesize by dual templating with soft templates. By using this method, one of the templates is responsible for the formation of zeolite framework and another template is for the formation of mesoporous. Previous study illustrated the synthesis of mesoporous ZSM-5 using dual templates. The study has used CTAB in order to create mesopore channels while tetrapropylammonium (TPA) for the crystalline wall of ZSM-5 [14]. Another study has successfully synthesized a highly stable mesoporous molecular sieve with a structure similar to MCM-48 with the presence of TPA and CTAB [15].

The formation of mesoporous zeolites gives lots of advantages in many applications especially in various catalytic reactions. They are primarily useful in improving the catalytic performances of conventional zeolites that having only micropores [16]. Some examples of catalytic reactions that used mesoporous zeolites are cracking, alkylation, isomerization and hydrogenation [17]. Knoevenagel condensation reaction is another example of catalytic reactions being catalyzed by

mesoporous zeolites (alkaline X and Y zeolites) [18]. This reaction involved the condensation of carbonyl compounds with active methylene compounds that usually forming bulky molecules as products. Some important intermediates produced from Knoevenagel condensation reactions have significant applications in industries such as therapeutic drugs, perfumes and cosmetics [19].

1.2   Problem Statement

In catalytic applications, the uses of zeolites are limited by slow diffusion of reactants into their micropores for bulky reactions. To solve the problem, many studies have focused on synthesizing a zeolite with proper pore size in order to accelerate the conversion of bulky molecules. One of the best strategies is by synthesizing mesoporous zeolites. Mesoporous zeolites offered some advantages such as fast diffusion and accessible for bulky molecules [20].

Recently, most studies were focused on synthesizing high silica mesoporous zeolites which are useful for acid-catalyzed reactions. It is therefore interest to synthesize a high aluminium-containing mesoporous zeolite that exhibited a basicity that could be used for base-catalyzed reactions. At present, sodalite (SOD) is an example of basic zeolite with high aluminium content (Si/Al = 1) and high stability in basic solution. However, the framework structure of SOD consists of a six membered ring with small pore openings size about 2.8 Å. Because of its small pores size, only small molecules such as helium (He), hydrogen (H) and water (H_2O) can go into the pore of SOD. The sole presence of micropores then limits the role of SOD's as catalysts for the reaction that involving bulky molecules [21].

The Knoevenagel condensation is an organic reaction between an aldehyde or ketone with an activated methylene to produce a substituted olefin. A base is commonly used to catalyze the reaction. Instead of using small reactants, this reaction can also be modified using large or bulky reactants. Since the SOD is a basic zeolite, it can be used as basic catalyst in Knoevenagel condensation reaction.

However, the presence of micropores in its structure limited only to the reaction involving small reactants. Therefore, this study is expected to solve the problem by synthesizing mesoporous SOD in order to catalyze Knoevenagel condensation reaction involving large or bulky reactants.

1.3   Objectives of Study

The objectives of this study are:

1. To synthesize mesoporous SOD by mixing of tetrapropylammonium (TPA) with various quaternary ammonium cations,
2. To characterize the synthesized mesoporous SOD,
3. To study the basicity properties of the synthesized mesoporous SOD,
4. To test the catalytic activity of the synthesized mesoporous SOD as a base catalyst in the Knoevenagel condensation reaction.

1.4   Scopes/Limitations of Study

This study focused on the direct synthesis of mesoporous SOD by dual templates approach. Sodium aluminate ($NaAlO_2$) was used as the source of alumina while fumed silica was used as the source of silica. Meanwhile, sodium hydroxide (NaOH) was used as alkali and counter ion sources in this study. For synthesis mesoporous SOD's, different quaternary ammonium cations such as dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (organosilane), cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB) and dimethyldioctadecylammonium bromide (DDAB) were used as mesotemplates and mixed with tetrapropylammonium (TPA). Besides, the synthesis of microporous SOD (Na-SOD) was done using the same method as in the preparation of mesoporous SOD's except without the presence of templates.

The resulting SOD samples were characterized using three techniques which were X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and nitrogen (N_2) adsorption-desorption measurement. While, the basicity properties of all SOD samples were studied by Hammett indicators test and back titration method. Besides, the basicity of successfully mesoporous SOD formed was compared with the synthesized microporous SOD (Na-SOD) using temperature programmed desorption of carbon dioxide (TPD-CO_2) technique.

The catalytic testing for all SOD samples was carried out in the Knoevenagel condensation reaction. The reaction of benzaldehyde with diethyl malonate was selected as a model of the reaction. Products of the reaction were separated using gas chromatography (GC) and determined by gas chromatography-mass spectroscopy (GC-MS). Evaluation of catalysts reactivity in term of percentages of conversion and selectivity were studied from the reaction.

1.5   Significances of Study

A new mesoporous SOD were successfully synthesized. By having larger size of pores, mesoporous SOD could be used to catalyze reaction involving larger molecules. In addition, mesoporous SOD could be further modified and used as a heterogeneous bases catalyst in others organic synthesis. Mesoporous SOD also may meet environmentally friendly practice that can reduce toxicity waste as compared with the conventional homogenous catalysts.

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