MICROWAVE SYNTHESIS OF SODALITE FROM COAL FLY ASH AS SOLID BASE CATALYST FOR KNOEVENAGEL REACTION

MOHD HILMI BIN MOHAMED

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To whom support me till the end.

Especially my parents

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ABSTRACT

Coal fly ash (CFA) is a waste product from burning of coal fuel in the electrical power plant. It contains mostly silica and alumina which in powder form is considered hazardous material but can be utilized as precursor for the synthesis of zeolite. In this study, CFA has been converted to sodalite (SOD) and tested as a base catalyst in Knoevenagel reaction. Sodalite has been synthesized using microwave heating by varying alkaline concentration and heating time to obtain optimum parameter for formation of pure sodalite. The synthesis was also conducted by conventional oven heating for comparision. All synthesized products were characterized with XRD, FTIR, FESEM and ^{29}Si MAS NMR. The results showed that quite pure sodalite (Na-SOD) crystal has been formed in 45 min by microwave heating as compared to 5 days by conventional oven heating. ^{29}Si MAS NMR showed the synthesized SOD has Si/Al ratio of 1 while FESEM gave irregularly-shaped crystal with the size ranging between 60 – 120 nm.The synthesized Na-SOD was ion exchanged with group 1 (K, Cs) and group 2 (Ca, Sr, Ba) metal ions in order to enhance sodalite basicity. The crystallinity of ion exchanged-SOD samples has decreased to ~ 70% and ~30% for samples exchanged with group 1 and group 2 metal ions, respectively. The catalytic testing of the catalysts in Knoevenagel reaction of benzaldehyde and dimethyl malonate was carried out, producing dimethyl-2-benzylidemalonate, methyl cinnamate and dimethyl-2,2-bis(hydroxyl(phenyl)methyl) malonate. Based on the conversion of reactant, K-SOD has shown the most active for the Knoevenagel reaction while Ca-SOD gave the lowest conversion. For the catalyst reusability, Cs-SOD gave the best performance in long-term application. The formation of dimethyl-2,2-bis(hydroxyl(phenyl)methyl) malonate as one of the products in this Knoevenagel reaction indicate that sodalite-based catalyst was highly basic but a non-selective catalyst.

ABSTRAK

Abu terbang batu arang (CFA) adalah bahan buangan daripada pembakaran arang dalam stesen janakuasa elektrik. CFA mengandungi sebahagian besar silika dan alumina yang boleh digunakan sebagai bahan mentah untuk sintesis zeolit. Dalam kajian ini, CFA telah ditukarkan ke sodalit (SOD) dan diuji sebagai mangkin bes dalam tindak balas Knoevenagel. Sodalit disintesis secara pemanasan gelombang mikro dengan dipelbagaikan kepekatan alkali dan masa pemanasan untuk mendapatkan parameter optimum bagi pembentukan sodalit tulen. Sintesis juga dijalankan menggunakan pemanasan ketuhar biasa sebagai perbandingan. Semua produk yang disintesis dicirikan dengan XRD, FTIR, FESEM dan ^{29}Si MAS NMR. Keputusan menunjukkan hablur sodalit (Na-SOD) hampir tulen telah terhasil dalam 45 min menggunakan pemanasan gelombang mikro berbanding 5 hari menggunakan pemanasan ketuhar. ^{29}Si MAS NMR menunjukkan SOD yang disintesis mempunyai nisbah Si/Al bersamaan dengan 1 manakala FESEM menunjukkan hablur tidak sekata dengan saiz dalam lingkungan 60-120 nm. Na-SOD yang telah disintesis mengalami pertukaran ion dengan ion logam kumpulan 1 (K, Cs) dan kumpulan 2 (Ca, Sr, Ba) untuk meningkatkan tahap bes bagi tindak balas Knoevenagel. Kehabluran SOD yang ditukar ion menurun kepada 70% dan 30% untuk sampel yang mengalami pertukaran dengan logam kumpulan 1 dan 2. Ujian mangkin berasaskan-SOD dalam tindak balas Knoevenagel antara benzaldehid dan dimetil malonat telah dilakukan untuk menghasilkan dimetil-2-benzilidenemalonat, metil cinnamat dan dimetil-2,2-bis(hidroksi(fenil)metil) malonat. Berdasarkan peratus pertukaran tindak balas, K-SOD menunjukkan mangkin paling aktif manakala Ca-SOD memberikan pertukaran paling rendah. Kebolehgunaan semula mangkin menunjukkan Cs-SOD memberikan prestasi terbaik dalam penggunaan jangka panjang. Berdasarkan pembentukan produk dimetil-2,2-bis(hidroksi(fenil)metil) malonat sebagai salah satu produk dalam tindak balas Knoevenagel menunjukkan mangkin berasaskan sodalit mempunyai sifat bes yang tinggi, tetapi mangkin tak berkepilihan.

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ABBREVIATIONS

CFA	Coal fly ash
CuKα	X-ray diffraction from copper Kα energy levels
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
XRD	X-ray diffraction
2θ	Bragg angle
NaOH	Sodium hydroxide
CH_3COOK	Potassium acetate
$CsNO_3$	Cesium nitrate
$CaCl_2$	Calcium chloride
$Sr(NO_3)_2$	Strontium nitrate
KBr	Potassium Bromide
GC	Gas chromatography

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Each year, tons of coal fly ash (CFA) has been produced as a waste product by the power plant that used coal as their main power source. Coal combustion gives by product in an estimation of about 600 million tons worldwide [1, 2]. A large number of portions of this production are coal fly ash (CFA).

Coal ash could be categorized into two forms. The top is fly ash while the bottom part is bottom ash or slag. Fly ash is collected at the top by using cyclones, electric precipitators or mechanical filters [3]. The percentage of fly ash generated in the combustion was 84% of total coal ash burned. The fly ash collected could have high percentage of silica sources. Silica sources from waste are very useful in many areas of research. Fly ash is also utilized in construction, low-cost adsorbent for removal of organic compound, flue gas and metals, lightweight aggregate, mine back fill, road sub-base and zeolite synthesis [1].

CFA has been used as a precursor in producing zeolite material [4-8]. Most of the zeolitic material mainly contains silica and alumina. This put a strong position for researches to be done with the composition of both materials. The composition of both components is useful in the production of zeolite material from a waste product [9-12]. In addition, this could reduce the usage of alumina as the Al source. The alumina usually applied while using silica as the precursor. The decrease usage of the alumina could decrease the cost of producing zeolite material. Table 1.1 shows the evolution of the molecular sieve materials.

Table 1.1: Evolution of molecular sieve materials [13].

Time of Initial Discovery	Composition
Late 40's to Early 50's	Low Si/A1 Ratio Zeolites
Mid 50's to late 60's	High Si/A1 Ratio Zeolites
Early 70's	SiO_2 Molecular Sieves
Late 70's	$A1PO_4$ Molecular Sieves
Late 70's to Early 80's	SAPO and MeAPO1 Molecular Sieves
Late 70's	Metallo-silicates, Aluminosilicates
Early to Mid 80's	$A1PO_4$-based Molecular Sieves
Early to Mid 90's	Metallophosphates Mesoporous Molecular Sieves Octahedral-tetrahedral Frameworks

Since CFA is silica rich waste, many researches has been done on the synthesis of zeolite. Due to its composition, many researchers propose detailed method in synthesizing zeolite from CFA. Until then, several methods such as hydrothermal, two-step processes and microwave-assisted were effective to produce zeolites from CFA [1, 4, 5, 7, 9, 11, 14, 15]. Basically, the proposed method was usually in the utilization of the hydrothermal method. Beside that, the zeolite synthesized from CFA also quite difficult to control because CFA contain a lot of impurities. These factors were quite challenging in order to determine which type of zeolite could be produced from CFA.

The interest of zeolites and zeotypes materials remain as the main interest in research field due to the organized TO_4 tetrahedral structure in such a way micropore are formed [16]. It is possible to have a large number of zeolites that differs in pore diameter, shape and topology. On top of that, it is important to understand the fundamentals of zeolite synthesis. It is due to the basic formation includes several condition such as type of solution, heating rate and rate formation of zeolite. On the other hand, the explanations of the general models of synthesizing zeolites are important in order to produce complicated reaction and crystallization system.

Zeolite is commonly synthesized by hydrothermal method, where the source of heating is from the oven and hot plate. In this conventional heating, the synthesis of zeolite usually takes longer time depending on the type of zeolite being produced with the developed technology. Inada *et. al*.[12] reported the synthesis of zeolite using microwave assisted hydrothermal which took 2 hours of microwave heating as compared to 3 days by conventional heating. This proved that microwave heating is more effective in terms of time to synthesis zeolite.

The modification of zeolite has also being studied in detail [17]. Depending on the type of zeolite, the active site of the zeolite promotes either basic or acid properties. The properties largely depend on the number of alumina on the zeolite itself. Siliceous zeolites are favourable to act as acid catalyst while the alumina rich tends to act as base catalyst. Based on which type of zeolite being synthesized, the sufficient amount of Si and Al were controlled throughout the process.

A review by Ahmaruzzaman [1] stated that many patents proposed different hydrothermal activation methods for further application in zeolite synthesis. This methodology is based on the dissolution of Al-Si bearing fly ash phase with alkaline solutions. The limitation, which is the speed of reaction were one of the barriers. High temperature will speed up the reaction by shortening the activation time. Nevertheless, to achieve the high temperatures will require higher cost. Microwave is a better alternative for a fast activation time and low in cost.

As-synthesized zeolites are usually in the form of Na-sodalite, where the counter ion is Na^+. In this state, zeolite has basic properties such that it can be applied as base catalyst in reaction that require base to proceed [7, 18]. Hence, it can be applied as a catalyst for process that need base catalyst such as Knoevenagel condensation reaction. Furthermore the reactivity of the catalysts is important in order to determine which catalyst is the most effective.

The zeolite also could undergo alteration. Alteration process requires a certain amount of metal that could be impregnated or ion-exchanged. Therefore, the zeolite also will have slight difference in the properties and characters. Further modification of zeolite could alter the property that is suitable for further application. However, not all zeolites are applicable due to the zeolite family has many Si-O-Al configurations. For example, large pore zeolite such as zeolite Y containing Na^+ could be exchange with Cs^+ ion without experiencing loss of crystallinity. Small pore zeolite such as Na-A experienced loss of crystallinity due to the Cs^+ ion has covered the surface area of the sodalite, thus generating larger basic site.

Knoevenagel reaction is a reaction that consists of reactions between series of aldehydes and active methylene groups. The products of the reaction are important towards many further applications, such as pharmaceutical and food industries [19-22]. In addition, the zeolite also could act as solid solvent. Therefore, the usage of solvent is less and the end product also easily controlled.

The advantage of using solid base as catalyst is the catalyst has reusability properties. The reusability applied to ensure the catalyst could be used in the long-term process. However, the catalysts also have their own limitations. The reusability contributes into lower percent conversion after a certain period. The major factors that lower the percent conversion is the poisoning. Poisoning of the catalyst active site does eliminate the site to undergone reaction. For example, the reaction produces H^+ ion will replace the base site on the zeolite.

1.2 Problem Statement

A lot of fly ash produced each year. The fly ash is hazardous to living things since it has high percentage of inorganic compounds, such as heavy metals. The difficulty to decompose the fly ash also gives a lot of problems. In order to decrease the effect of fly ash towards environment, utilizing the waste fly ash is going to be a challenging task.

CFA contains certain composition of silica and alumina as major components. However, the silica in CFA is in the form of quartz as the dominant phase. Quartz is the most stable SiO_2 crystal phase compare to other form of SiO_2

crystal phase and thus it is difficult to dissolve even in highly alkaline medium. For zeolite formation, the main compositions of the framework are silica and alumina both must be dissolved form in order to form the framework of aluminosilicate zeolite. Because of the difficulties of quartz in CFA to dissolve, it limits its ability to be used as silica source in the formation of zeolite. In order to overcome this problem, several parameters have to be studied such as heating method. Previous work has reported the use of microwave conversion of CFA to produce single phase zeolite but mostly the product in the mixture of phases. Thus, this study attempts to focus on conversion of CFA to zeolite of single phase.

Conventional method of synthesizing zeolite involved direct heating in oven. Hence, make it difficult to control the product in hydrothermal method since it requires longer time of crystallization. Instead of using conventional oven, microwave promise a new approach in the synthesis of zeolite from CFA since not many work has been reported in the direct conversion of CFA to zeolite by microwave heating. Thus, a lot study can be explored to utilize this method especially to produce pure zeolite from CFA. The microwave heating could dissolve the stable quartz for the formation of dissolved silicate ion that necessary for the formation of the Si-O-Al bonding of the zeolite framework.

Since the zeolite produced form the CFA will be high in Na content, it can be used as basic catalyst in Knoevenagel reaction. Industrially, Knoevenagel reaction mainly applied in pharmaceutical industries because the product from the reaction is having carbon double bond compound. The carbon double bond with benzene ring on the structure could act as the starting material for several applications. The carbon double bond could easily react with many substances to produce useful products in our daily lives.

1.3 Research Objectives

The objectives of this research are:

1. To utilize the microwave as a tool to synthesize sodalite from CFA
2. To modify zeolite obtained with alkaline and alkaline earth metal ions.
3. To study the physiochemical properties of zeolite formed.
4. To test the activity of sodalite catalyst as base catalyst in Knoevenagel reaction.

1.4 Scope of the Research

This study involved conventional oven heating and microwave heating to synthesize zeolite from CFA. CFA used in this study was obtained from Kapar power station located in Klang, Selangor. NaOH pellets were used as alkali and counter ion sources in this study. The concentrations of NaOH were varied between 3M to 5M. For conventional synthesis, constant time of heating of 5 days was used. In the microwave synthesis, the heating time was from 15 minutes to less than 1 hour due to the vigorous heating inside the microwave oven. The concentration of NaOH for microwave heating ranging between 2 M and 4 M. Apart from that, there were additions of sodium aluminate in order to increase the ratio of alumina in the raw CFA. The alumina was added to ensure the alumina and silica content on the gel mixture was 1 to 1.

The ion-exchange process was done on the as-synthesized zeolite obtained from the conversion of CFA to zeolite. The sample was ion exchanged with group 1 and group 2 metal ions. Ion exchanged was performed at various temperature in order to ensure the crystallinity did nit decrease too much due to the leaching of the silica during the ion exchange process.

Knoevenagel reaction was selected for the reaction between benzaldehyde and dimethyl malonate . The active methylene group on the dimethyl malonate was less studied by other researchers. The effort to utilize the zeolite as the catalyst was needed to ensure the applicability in catalyst field. The zeolite opens up a good chance to convert the reactant into product. Meanwhile, the conversion percentage plays important role to determine the reactivity of the catalyst. However, the catalyst also has its own selectivity. Different catalyst will yield different major and minor compounds according to their properties. The modification on the catalyst plays important role in yielding the major product and minor product in the reaction.

All synthesized and modified samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), 29Si MAS nuclear magnetic resonance (NMR) and field emission scanning electron microscopy (FESEM). Gravimetric analysis was used to determine the amount of the dissolved quartz available after certain time of synthesis time. Elemental analysis was determined by using flame photometer and EDX. Basicity studies were performed by using TPD-CO_2 desorption. The sample then was used as base catalyst in Knoevenagel condensation reaction between benzaldehyde and dimethyl malonate. Product obtained were characterized by using gas chromatography and component were characterized by GC-MSD

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