SYNTHESIS OF ZEOLITE FERRIERITE FROM RICE HUSK ASH, CHARACTERIZATION AND ACTIVITY TOWARDS FRIEDEL-CRAFTS ACYLATION FOR THE FORMATION OF *p*-METHOXYPROPIOPHENONE

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Teristimewa buat:
mak, Amnah Mohd Nor, abah, Bahruji Abdullah dan keluarga,
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semoga usaha ini diredhaiNya

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ABSTRACT

Rice husk ash (RHA) consisting more than 90% of amorphous silica obtained under controlled burning of rice husk was directly used in the synthesis of ferrierite type-zeolite. The synthesis was performed under hydrothermal condition in the presence of different organic templates, oxide compositions and at various crystallization periods. Solid products obtained from the synthesis were characterized by XRD, FTIR, ^{29}Si MAS NMR, N_2 (g) adsorption and SEM techniques. Results showed that pure ferrierite can be formed from the initial molar oxide ratios in the range of 1.31 – 1.5 Na_2O : Al_2O_3 : 10 – 30 SiO_2 : 4 – 10.0 template : 410 H_2O with only pyrrolidine (Py) as the organic template. In general, quartz was obtained at higher SiO_2/Al_2O_3 and lower Py/Al_2O_3 ratios. The crystal phase changes from ferrierite to analcime and lastly to quartz, with increasing SiO_2/Py ratios. RHA was directly transformed to ferrierite phase within one day and reached equilibrium after 4 days crystallization. The acidity study of the H-ferrierite samples at different SiO_2/Al_2O_3 ratios (12, 20 and 30) using IR-pyridine adsorption method showed the increase of acid sites with the decrease of SiO_2/Al_2O_3 ratios in ferrierite framework. In each case, the Brønsted acid site is higher than Lewis acid sites. The catalytic activity of ferrierite at different SiO_2/Al_2O_3 ratios towards Friedel-Crafts reaction between anisole and acid anhydrides was investigated. Results from the catalytic activity showed that only *p*-methoxypropiophenone and propionic acid was produced as the main product and side product respectively when propionic acid was used as acylating agent. The optimum temperature for the reaction was 120^{o}C and ferrierite catalyst with SiO_2/Al_2O_3 ratio 12 gave the highest conversion of anisole (66 %) and the selectivity of the main product (80 %). When acetic anhydride was employed as acylating agent, the conversion of anisole (55 %) and the selectivity of desired product (98 %) showed a higher percentage as compared with propionic anhydride. In both cases, the main product obtained is in *para* orientations with higher selectivity proved that H-ferrierite is a selective catalyst for the production of *para* orientation products.

ABSTRAK

Abu sekam padi (RHA) mengandungi lebih daripada 90% silika amorfus yang diperolehi daripada pembakaran terkawal digunakan untuk menyediakan zeolit ferrierit. Sintesis dijalankan secara hidroterma dengan mengubah pelbagai templat organik, nisbah komposisi oksida dan masa penghabluran. Hasil pepejal yang diperolehi di cirikan dengan menggunakan kaedah XRD, FTIR, ^{29}Si MAS NMR, penjerapan N_2(g) dan SEM. Keputusan menunjukkan ferrierit tulen telah berjaya disintesis dalam julat 1.31 – 1.5 Na_2O : Al_2O_3 : 10 – 30 SiO_2 : 4 – 10.0 templat : 410 H_2O dengan hanya menggunakan pyrrolidin (Py) sebagai templat organik. Apabila nisbah SiO_2/Al_2O_3 ditingkatkan dan nisbah Py/Al_2O_3 direndahkan, tindakbalas akan menghasilkan kuartz. Fasa hablur berubah dari ferrierit kepada analsim dan diikuti oleh kuartz dengan pertambahan nisbah SiO_2/Py. Pembentukan zeolit ferrierit secara langsung daripada RHA berlaku dalam tempoh satu hari dan mencapai keseimbangan selepas 4 hari penghabluran. Kaedah penjerapan piridin – IR terhadap H-ferrierit dengan pelbagai nisbah SiO_2/Al_2O_3 (12, 20 dan 30) telah menunjukkan pertambahan tapak asid dengan berkurangnya nisbah SiO_2/Al_2O_3, tetapi bagi setiap sampel, kehadiran tapak asid Brønsted adalah lebih tinggi berbanding tapak asid Lewis. Keaktifan mangkin zeolit ferrierit telah dikaji terhadap tindak balas pengasilan Friedel-Crafts antara anisol dan asid anhidrida. Keputusan menunjukkan hanya *p*-metoksipropiofenon dan asid propionik terbentuk dengan masing-masing sebagai hasil utama dan hasil sampingan apabila propionik anhidrida digunakan sebagai agen pengasilan. Suhu optimum tindak balas adalah pada 120^{o}C dengan mangkin ferrierit pada nisbah SiO_2/Al_2O_3 12 memberikan peratus penukaran bagi anisol yang tertinggi dengan 66 % dan peratus kepilihan terhadap produk utama sebanyak 80%. Apabila asetik anhidrida digunakan sebagai agen pengasilan, peratus pertukaran anisol dan peratus kepilihan hasil utama meningkat berbanding propionik anhidrida sebagai agen pengasilan. Hasil utama yang terbentuk dalam kedua-dua tindak balas adalah dalam orientasi *para* dengan kepilihan yang tinggi, di mana ini membuktikan bahawa H-ferrierit adalah mangkin yang baik bagi menghasilkan sebatian dengan orientasi *para.*

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LIST OF SYMBOL / ABRREVIATIONS

RHA	-	rice husk ash
FER	-	Ferrierite
Py	-	pyrrolidine
Pn	-	piperidine
Gly	-	glycerol
GC	-	gas chromatography
H-Fer	-	ferrierite zeolite in hydrogen formed
H-Fer-12	-	ferrierite zeolite in hydrogen formed with SiO_2/Al_2O_3 ratio 12
Fer-12	-	ferrierite zeolite with SiO_2/Al_2O_3 ratio 12
Si-12	-	sample with SiO_2/Al_2O_3 ratio 12
N-5	-	sample with Na_2O/Al_2O_3 ratio 5
Py-10	-	sample with Py/Al_2O_3 ratio 10
Fer-12-0.25	-	sample Fer-12 with 0.25 day crystallization period
PBU	-	primary building unit
SBU	-	secondary building unit
TBU	-	tertiary building unit
GC	-	gas chromatography
BET	-	Brunaeur, Emmett, Teller
FS	-	fume silica
JBW	-	NaJ (Barrer and White)
MTBE	-	methyl tert-butyl ether
JCPDS	-	Joint-Committees on Powder Diffraction Standards

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

According to the Malaysian Budget 2005, Malaysia will focus on research and development activities, which can be divided into four main fields, including the finding of advanced materials. Zeolites that are classified under advanced materials show a higher demand in worldwide market, reaching around USD 2.15 billion per year in 2001 and is expected to increase to $2.52 billion by 2005 and 2.94 billion by 2010. The utilization of zeolite as catalysts in industrial processes occupies 40 % followed by the oxides, complex oxides and ion-exchange resins [Tanabe *et al.* 1999]. The average utilization worldwide for zeolite in fine chemicals industries is thought to be around 60% of its uses worldwide, either as a parent form or after its modification. Nowadays, zeolites are employed as alternative heterogeneous catalysts to substitute homogenous catalysts in many organic processes such as in Friedel-Crafts reaction because of its more efficient and environmentally-friendly which can eventually reduce plant corrosion and eliminate environmental problems.

The synthetic zeolites give alternative sources for natural zeolites in which it is exists in minor quantity and always in the mixture of other constituents makes natural zeolites unfavorable and uneconomical to be used for specific applications such as catalysts. Ferrierite for example only can be found in three places in the world [Nadimi, 1993]. Based on these, the research in the synthesis of zeolites and other mesoporous materials has been widely explored by researchers all around the world. Studies including the choice of raw materials, optimization of experimental

condition for synthesis and the modifications of zeolites structure are the step to increase the potential of zeolite in order to fulfill the market demand.

1.2 Research Background

The main synthesis component for preparing zeolite is silica besides aluminium, mineralized reagent and water. It is known that the rice husk ash contains silica in which the white ash contains up to 96 % to 99 %. The abundant rice husk ash in Malaysia is giving alternative economical sources for synthesizing zeolites. Several types of zeolites such as zeolite Y [Ramli, 1995], zeolite ZSM-5 [Rawtani *et al.* 1989] and zeolite β [Didik, 2001] have been prepared by using rice husk ash as silica source. The silica was used either directly or by extracting the silica from the ash. The encouraging results from previous works have prompted us to synthesize another type of zeolite namely ferrierite which has great potential as catalysts in organic synthesis as well as in the reduction of nitrous oxides gaseous. In this research, rice husk ash was directly used for the first time in the synthesis of ferrierite.

Synthetic ferrierite is being commercialized either as it is or in the modified form as catalysts in skeletal isomerization of n-alkenes and for reduction of nitrous oxides gaseous. The great potential of ferrierite as catalysts has been widely explored by researchers. Ferrierite with the unique bidimensional pore systems shows the best performance in the isomerization of alkenes for petrochemicals industry compared to other types of catalysts [Yokomori *et al*. 2001]. Recent uses of ferrierite in the form of metal-exchange ferrierite (Ce and Ar) are efficient catalysts for nitrous oxide gaseous reduction. The high selectivity of ferrierite towards NO_x reduction and the capability of Brønsted acid sites which promoted the activation of propene for the pairing with NO or NO_2, make ferrierite as a good catalyst for NO_x reduction [Seijger *et al.* 2003]. Nowadays, the capability of ferrierite as a hydrocarbon trap in automobile exhaust is still being explored by researchers in order to reduce the hydrocarbon emissions.

The great potential of ferrierite as catalysts whether in petrochemical industry or automobile and environment technology was encouraged in this study to prepare ferrierite in optimum conditions that can reduce the cost of ferrierite production. Usually, in the synthesis of ferrierite using commercial silica as silica sources requires high temperature and long crystallization period with the presence of certain amounts of template to ensure the formation of ferrierite. In this research, the use of rice husk ash as the substitute of commercial silica will lower the overall cost of ferrierite production in term of low cost of raw materials, short crystallization period than commercial silica and the low amount of template used. This study will focus in the optimization of ferrierite in order to find the optimum formulation for synthesizing ferrierite from rice husk ash. In order to cut down the cost of producing ferrierite, the small amount of template or free template system is needed. The template is the main component in the synthesis ferrierite that contributes almost 60% of the cost of zeolite production.

1.3 Objectives of research

The main objective of this research is to explore the capability of rice husk ash as raw material in the synthesis of ferrierite and also to obtain the optimum composition and synthesis conditions for ferrierite. As ferrierite is classified as a medium pore zeolite and having both Lewis and Brønsted acid sites, the potential of ferrierite for Friedel-Crafts acylation was also explored. The objectives of this research are listed as follows:

1. To synthesize ferrierite using rice husk ash as silica source
2. To optimize the metal oxides composition of the initial gel in ferrierite synthesis and the reaction conditions
3. To study the transformation of rice husk ash to ferrierite
4. To test the reactivity of the as-synthesized ferrierite as catalyst in the Friedel-Crafts acylations.

1.4 Scope of the Research

The work reported in this study focuses on the synthesis of ferrierite using amorphous rice husk ash which was obtained by controlled burning of rice husk, as silica sources. Several templates namely pyrolidine, piperidine and ethylenediamine were used in the synthesis. The templates that gave the best ferrierite were chosen for the optimization study of preparing ferrierite from rice husk ash.

The initial oxides compositions were varied to obtain the ranges of oxides that can produce pure ferrierite. The transformation study of rice husk ash to ferrierite was performed at different crystallization period starting from 0 up to 12 days of crystallization. Characterization of each sample was carried out using Fourier Transform Infared (FTIR), X-ray Diffractogram (XRD), ^{29}Si Magic Angle Spinning NMR (MAS NMR), Scanning Electron Microscopy (SEM), N_2 (g) adsorption and also the weight of the sample at the end of each crystallization time.

Modification of the as-synthesized ferrierite to the hydrogen form of ferrierite was carried out by ion exchanged with NH_4Cl solution followed by calcinations. The Si/Al ratio in ferrierite framework was measured using ^{29}Si MAS NMR and the acid strength and the type of acid sites were measured using Temperature Programmed Desorption (TPD) of ammonia and Fourier Transform Infrared spectroscopy (FTIR) using pyridine as the probe base molecule.

The final part in this study is to test the catalytic capability of ferrierite in hydrogen form from rice husk ash towards Friedel-craft acylation of anisole with propionic and acetic anhydride as the acylating agents. The reaction was performed in a batch reactor and the products were separated and analyzed by gas chromatography (GC) and the identification of products were carried out using gas chromatography with mass spectrometry detector (GC-MSD).

The activity study of H-ferrierite as catalyst in Friedel-Crafts acylation of anisole and both acid anhydride shows that H-ferrierite has a potential to be a selective *para* catalyst for producing only product with *para* orientation. All the H-ferrierite catalysts used, produced only *p*-methoxypropiophenone as a main product with propionic acid as the side product reaction. The conversion increased relatively with the decreasing SiO_2/Al_2O_3 ratios due to the increase in Brønsted acid sites in the ferrierite framework. Reactions that have been carried out under various periods show that the optimum reaction time is in the first four hours. The effect of reaction temperature study reveals that H-ferrierite gives the optimum performance when the temperature is 120^{o}C. From this study, it is suggested that the optimum reaction conditions for acylation of anisole with propionic anhydride is at 120^{o}C and for 4 hours. The effect of different size of acylating agent (acetic anhydride as compared with propionic anhydride) in acylation of anisole shows that the product obtained is also in *para* orientation. However, the product selectivity and the anisole conversion were 98 % and 55 %, were higher as compared to propionic anhydride. From the product obtained, we proposed that the mechanism of this reaction involved electrophile aromatic substitution which included the formation of acylium ions from the Brønsted acid sites in the catalysts.

5.2 Recommendation

The successful formation of ferrierite from rice husk ash proved the reactivity of the rice husk ash as silica source in the synthesis of zeolite ferrierite. Therefore, the study can be extended to produce ferrierite using rice husk ash with higher SiO_2/Al_2O_3 ratios or siliceous ferrierite. These materials are important precursor for producing mesoporous materials which are highly researched now. The modification of ferrierite from rice husk ash to mesoporous solid also can be done in order to vary the function of ferrierite as catalyst particularly for synthesizing larger organic molecules. Besides that, the study can be extended to investigate the potential of ferrierite from rice husk ash as catalysts in other reactions such as for the reduction of nitrous oxides gaseous. The utilizations of ferrierite as catalysts in the reductions of nitrous oxides gaseous have a potential to solve the problems arise while ammonia used as reducing agents. The application of ammonia is impeded by concern over safety and ammonia distribution logistics. The use of ferrierite from rice husk ash as catalysts also can be extended in the skeletal isomerization of n-alkenes which is the main potential utilization of ferrierite in the future industries.

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