SYNTHESIS AND CHARACTERIZATION OF SULPHATED AlMCM-41 AND ITS CATALYTIC ACTIVITY IN DIBENZOYLATION OF BIPHENYL WITH BENZOYL CHLORIDE

NG ENG POH

UNIVERSITI TEKNOLOGI MALAYSIA

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NG ENG POH

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For the Lord God Almighty,

My beloved family

And

My best friends

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PREFACE

This thesis is the result of my work carried out in the Department of Chemistry, Universiti Teknologi Malaysia between Jun 2002 to September 2004 under the supervision of Prof. Dr. Halimaton Handan. Part of my work described in this thesis has been reported in the following publications:

1. Ng Eng Poh, Hadi Nur, Mohd Nazlan Mohd Muhid and Halimaton Hamdan, (2005). "Sulphated AlMCM-41: Mesoporous Solid Brönsted Acid Catalyst for Dibenzoylation of Biphenyl", *Catalysis Today* (Accepted).

2. Ng Eng Poh and Halimaton Hamdan, (2005). "Structural Properties and Surface Acidity Characterization of Sulphated AlMCM-41", *Poster Presentation in International Science Congress (ISC), Putra World Trade Centre, Kuala Lumpur Malaysia*.

ABSTRACT

Benzoylation of biphenyl with benzoyl chloride is an important acylation reaction, producing monosubstituted product, 4-phenyl benzophenone (4-PBP) and disubstituted product, 4, 4'- dibenzoylbiphenyl (4, 4'-DBBP). 4, 4'-DBBP is a monomer used as a component in emitting layer in polymer light emitting (PLED) devices. The objective of this study is to synthesize and characterize a highly active sulphated AlMCM-41 acid catalyst by enhancing its acidity through sulphation. Firstly, the AlMCM-41 with various SiO_2/Al_2O_3 ratios was prepared by direct synthesis, followed by conversion to H-AlMCM-41 via ion exchange of NaAlMCM-41 with ammonium nitrate. Finally, sulphated AlMCM-41 was prepared by impregnation of sulphuric acid in toluene. The sulphated MCM-41 materials possess high surface area (>500 m^2/g) and large quantities of Brönsted acid sites after characterizing with surface analyzer and pyridine infrared spectroscopy. ^{27}Al MAS NMR indicates the presence of octahedrally coordinated extra-framework sulphated aluminiums (EFAL) and aluminium sulphate. The Hammett indicators show that the acid strength of the sulphated AlMCM-41 materials was stronger than sulphuric acid and H-AlMCM-41 because of sulphate groups attached to aluminium atom in sulphated AlMCM-41. The results of comparative study on the dibenzoylation of biphenyl reaction indicate that only sulphated AlMCM-41 gives both monosubstituted 4-PBP and disubstituted 4, 4'-DBBP with the highest activity compared to sulphuric acid, H-AlMCM-41 and sulphated amorphous silica.

ABSTRAK

Benzoilasi bifenil dengan benzoil klorida merupakan tindak balas pengasilan yang penting, menghasilkan hasil penukargantian mono, 4-fenil benzofenon (4-PBP) dan hasil penukargantian dwi, 4, 4'- dibenzoilbifenil (4, 4'-DBBP). 4, 4'-DBBP merupakan monomer yang digunakan dalam lapisan pemancaran dalam peranti pemancar cahaya polimer (PLED). Objektif kajian ini adalah untuk meningkatkan keasidan mangkin yang digunakan dalam tindak balas pemangkinan dwibenzoilasi bifenil melalui modifikasi H-AlMCM-41. AlMCM-41 dengan nisbah SiO_2/Al_2O_3 disintesiskan melalui kaedah sintesis secara langsung, diikuti dengan menukarkannya kepada bentuk H-AlMCM-41 melalui penukaran ion menggunakan ammonium nitrat. Akhirnya, AlMCM-41 tersulfat disediakan melalui kaedah pengisitepuan dengan asid sulfurik dalam toluena. Mangkin AlMCM-41 tersulfat mempunyai luas permukaan yang tinggi (>500 m^2/g) dan kuantiti tapak asid Brönsted yang banyak selepas dicirikan dengan penganalisis permukaan dan spektroskopi inframerah piridina. ^{27}Al MAS NMR menunjukkan kehadiran Al tersulfat luar bingkaian yang berkoordinatan oktahedra dan aluminium sulfat. Penunjuk Hammett menunjukkan bahan MCM-41 tersulfat mempunyai kekuatan asid yang lebih tinggi daripada asid sulfurik dan H-AlMCM-41. Keputusan tindak balas dwibenzoilasi bifenil menunjukkan bahawa hanya AlMCM-41 tersulfat memberikan hasil penukargantian mono (4-PBP) dan dwi (4, 4'-DBBP) dengan keaktifan tertinggi berbanding dengan asid sulfurik, H-AlMCM-41 dan silika amorfus tersulfat.

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LIST OF SYMBOL AND ABBREVIATIONS

MCM-41	-	Mobile Crystalline Material-41
RHA	-	Rice husk ash
Py	-	Pyridine
i.e.	-	Id est (that is)
BET	-	Brunauer-Emmett-Teller
GC	-	Gas chromatography
Å	-	Angstrom (10^{-10} meters)
kV	-	Kilovolts
α	-	Alpha
β	-	Beta
PDPV	-	Poly (4, 4'-diphenylene diphenylvinylene)
LED	-	Light emitting devices
IUPAC	-	International Union of Pure Applied Chemistry
LCT	-	Liquid-crystal templating
n	-	Diffraction order from n = 1, 2, 3, ….
d	-	Distance
2D	-	Two dimensions
λ	-	Lambda
θ	-	Theta
δ	-	Delta
FTIR	-	Fourier transform infrared
NMR	-	Nuclear magnetic resonance
MAS	-	Magic angle spinning
CP	-	Cross polarization
EFAL	-	Extra-framework aluminium
ppm	-	Part per million

%	-	Percent
~	-	Approximately
TG/DTA	-	Thermogravimetric and Differential Thermal Analysis
TGA	-	Thermogravimetric Analysis
DTA	-	Differential Thermal Analysis
H_o	-	Hammett acidity function
μL	-	Microlitre
MS	-	Mass spectrometry
GC-MS	-	Gas chromatography combined with mass spectrometry
4-PBP	-	4-Phenyl benzophenone
4, 4'-DBBP	-	4, 4'-dibenzoylbiphenyl
CTABr	-	Cetyltrimethylammonium bromide
NH_4OH	-	Ammonium hydroxide
min	-	Minute
^oC	-	Celsius
h	-	Hour
wt%	-	Weight percent
g	-	Gram
mg	-	milligram
SiO_2/Al_2O_3	-	Silica over alumina ratio
mol	-	Mole
mmol	-	Millimole
m.p.	-	Melting point
mA	-	Milliampere
^{o}	-	Degree
cm^{-1}	-	Per centimeter
UNCAL-1	-	Uncalcined MCM-41 with SiO_2/Al_2O_3 ratio ∞
UNCAL-2	-	Uncalcined AlMCM-41 with SiO_2/Al_2O_3 ratio 60
UNCAL-3	-	Uncalcined AlMCM-41 with SiO_2/Al_2O_3 ratio 30
UNCAL-4	-	Uncalcined AlMCM-41 with SiO_2/Al_2O_3 ratio 15
CAL-1	-	Calcined MCM-41 with SiO_2/Al_2O_3 ratio ∞
CAL-2	-	Calcined AlMCM-41 with SiO_2/Al_2O_3 ratio 60

CAL-3	-	Calcined AlMCM-41 with SiO_2/Al_2O_3 ratio 30
CAL-4	-	Calcined AlMCM-41 with SiO_2/Al_2O_3 ratio 15
HCAL-1	-	Protonated MCM-41 with SiO_2/Al_2O_3 ratio ∞
HCAL-2	-	Protonated AlMCM-41 with SiO_2/Al_2O_3 ratio 60
HCAL-3	-	Protonated AlMCM-41 with SiO_2/Al_2O_3 ratio 30
HCAL-4	-	Protonated AlMCM-41 with SiO_2/Al_2O_3 ratio 15
SCAL-1	-	Sulphated MCM-41 with SiO_2/Al_2O_3 ratio ∞
SCAL-2	-	Sulphated AlMCM-41 with SiO_2/Al_2O_3 ratio 60
SCAL-3	-	Sulphated AlMCM-41 with SiO_2/Al_2O_3 ratio 30
SCAL-4	-	Sulphated AlMCM-41 with SiO_2/Al_2O_3 ratio 15
MHz	-	Megahertz
μs	-	Microsecond
TMS	-	Tetramethyl silane
BJH	-	Barrett, Joyner, Halenda
mbar	-	millibar
kPa	-	Kilopascal
m/z	-	Mass over charge
a_o	-	Unit cell parameters
t	-	Crystallite size
W_d	-	Pore diameter
b_d	-	Pore wall thickness

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CHAPTER 1

INTRODUCTION

1.1 Research Background and Problem Statement

Catalyst is defined as a substance that increases the rate of reaction without being appreciably consumed in the process [1]. Catalyst increases the reaction rate by offering other route of reaction with lower activation energy of the reaction system. There are many chemical reactions which need this substance in order to enhance the reaction rate. The presence of this substance is essential not only for enhancing reaction rate but also decreasing energy consumption and minimizing the waste production.

Today, catalysts play a vital role in the chemical industries, with a total contribution of ~20% of world GNP [2]. Apart from that, there are approximately 80% of the industrial reactions such as acylation, oxidation, hydrogenation, epoxidation etc. use catalysts. Among the reactions, Friedel-Crafts acylation (benzoylation) reaction is of interest in industries due to the importance of preparing aromatic ketones as intermediate in the dyes [3], pharmaceutical and fragrance [4] industries. An example of benzoylation reaction which has been studied is the benzoylation of biphenyl with benzoyl chloride [5-8]. More attention has been centered on it because of its applications. The monosubstituted product, 4-benzoylbiphenyl or 4-phenyl benzophenone (4-PBP) is used in the synthesis of antifungal bifonazole agent [7]. The 4-PBP is also an intermediate in the synthesis of fructone, an apple scent used in fragrant, detergents [9] and photo initiator [7] whereas the disubstituted product, 4, 4’- dibenzoylbiphenyl (4, 4’-DBBP) is used as a monomer in producing poly (4, 4'-diphenylene diphenylvinylene) or PDPV, an attractive polymer for electroluminescence because it has very high photoluminescence efficiency in solid state along with good solubility in common organic solvents [10]. As a result, it is used as an emitting layer in polymer light emitting (PLED) [11].

Liquid phase Friedel-Crafts reactions traditionally have been catalyzed by strong Brönsted acids such as CF_3SO_3H, FSO_3H, H_2SO_4 and HF and by soluble Lewis acids such as $TiCl_4$, $AlCl_3$ and $FeCl_3$ [12]. These acids are very strong in terms of their catalytic activity. Unfortunately, some of the homogeneous catalysts such as $TiCl_4$, $AlCl_3$ and $FeCl_3$ are highly sensitive to moisture, corrosive and environmentally unfriendly [13]. In industrial processes, the reaction brings another disadvantage to this system where it has a difficulty in product purification due to production of large amount of side products [14]. Therefore, a demand for searching an alternative is a need to overcome this problem.

Recently, the use of solid acid catalysts such as zeolites [3, 4, 7] and mesoporous materials [15, 16] has been reported for the acylation reaction. Zeolites and mesoporous materials are known for their shape selective properties and they have been used widely in a variety of acid and base catalyzed shape selective reactions. In addition, these materials are easy to separate from the product, environmentally unfriendly, small amount of hazardous corrosive wastes, high catalyst reusability, high thermostability, safer and easier to handle [14, 17].

Current research on the production of 4, 4'-DBBP via homogeneous and heterogeneous systems is still facing difficulties. For example, Walczak et al. [15] were only able to prepare 4-PBP in 74% of yield by treatment of benzoyl chloride with $AlCl_3$ in chloroform at room temperature, followed by addition of biphenyl into refluxing solution, Equation 1.1. Another researchers, viz. Han et al. [7] synthesized 94.2 % yield of 4-PBP by stirring benzoyl chloride with biphenyl and $AlCl_3$ in the presence of nitrobenzene at 120 ^{o}C, Equation 1.2.

Benzoyl chloride + $AlCl_3$ $\xrightarrow[\text{Reflux in } CHCl_3 \text{ at } 25\ ^oC]{+\text{ Biphenyl}}$ 4-PBP (74%) (Equation 1.1)

Benzoyl chloride + Biphenyl $\xrightarrow[\text{Reflux in } PhNO_2 \text{ at } 120\ ^oC]{+\ AlCl_3}$ 4-PBP (94.2%) (Equation 1.2)

Recently, the first attempt to synthesize 4, 4'-DBBP using H-AlMCM-41 as heterogeneous catalyst with 100% selectivity was reported, however with very low conversion (0.05%) [5]. According to the researchers, these unsatisfactory results might be due to low amount of Brönsted and Lewis acid sites as well as its acid strength. In addition, the reaction condition such as effect of temperature, solvent used, reactants and catalyst loaded also contribute to these results. In view from the above, it is of importance to (i) develop a new catalyst or modify the existing catalyst in order to enhance the amount and the strength of acidity of the materials and (ii) improve reaction condition for the selective synthesis of 4, 4'-DBBP. By taking the actions suggested, it is expected that the activity of the catalyst will be improved. Figure 1.3 shows two possible routes to drive the reaction to obtain targeted product 4, 4'-DBBP either via direct or consecutive route.

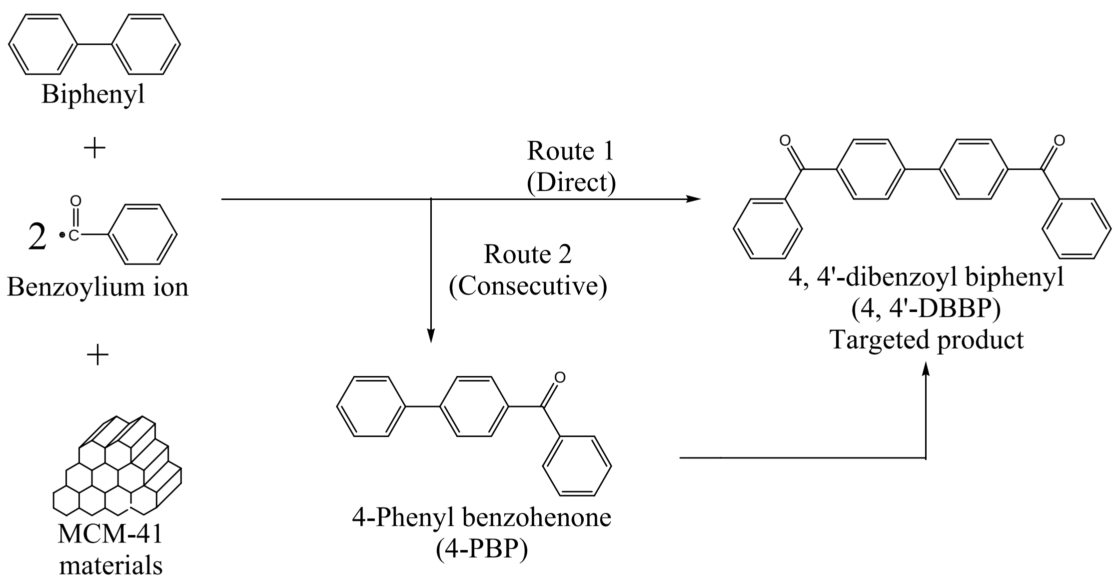


Figure 1.1: Two proposed reaction routes: Route1 (direct) and Route 2 (consecutive) synthesis of the dibenzoylation of biphenyl using sulphated AlMCM-41 mesoporous materials and benzoyl chloride.

1.2 Objectives of Research

The objectives of the research are:

1. To synthesize and characterize a highly active sulphated AlMCM-41 heterogeneous acid catalyst.
2. To relate the acidity to the structural characteristic of the catalyst.
3. To study the catalytic properties of the developed catalyst in dibenzoylation of biphenyl reaction (model reaction).
4. To study the effect of reaction parameters on the production of 4, 4'-DBBP.

1.3 Research Strategies

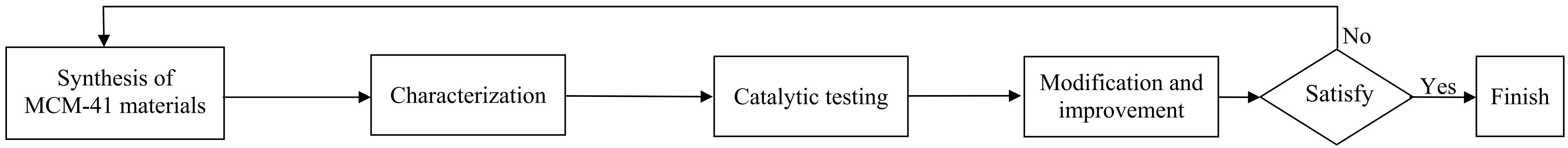
The flow diagram shown in Figure 1.2 describes about research strategies. Generally the studies involve synthesis, modification, catalytic testing and optimization. Characterizations are carried out by various techniques as listed. The catalytic activity was tested in a model reaction – dibenzoylation of biphenyl reaction. The modification, characterization and catalytic activity testing processes were repeated until a suitable catalyst was discovered.

1.4 Scope of Research

The work reported in this study focuses on the synthesis of sulphated AlMCM-41 with various of SiO_2/Al_2O_3 ratio using amorphous rice husk ash as silica source and sodium aluminate as aluminium source. MCM-41's template namely cetyltrimethyl ammonium bromide (CTABr) was used as structure directing agent. The modification was followed by conversion to H-AlMCM-41 via ion exchange of NaAlMCM-41 with ammonium nitrate solution followed by calcination and lastly impregnated with sulphuric acid in order to obtain sulphated AlMCM-41.

Characterization of each sample was carried out using Fourier Transform Infared (FTIR) spectrometer to study the molecular bondings while the crystalinity and crystallite size of the samples were analyzed by means of X-ray Diffraction analysis (XRD). Furthermore, characterization of the samples was also conducted using ^{29}Si and ^{27}Al Magic Angle Spinning NMR (MAS NMR) spectrometers to study the silicon and aluminum environments in the structure whereas the textural properties such as specific surface area, pore volume, pore diameter and pore wall thickness was measured by using nitrogen gas adsorption-desorption analysis. The thermal stability and volatile matter in the MCM-41 samples were determined by utilizing thermogravimetry and differential thermal analysis. The acid strength and the type of acid sites were measured using Hammett indicators 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 sulphated AlMCM-41 towards Friedel-craft dibenzoylation of biphenyl with benzoyl chloride as the benzoylating agents. The reaction was performed in a batch reactor and the products were separated and analyzed quantitatively by gas chromatography (GC) and the identification of products were carried out using gas chromatography with mass spectrometry detector (GC-MSD).



❖Synthesize catalysts in various SiO_2/Al_2O_3 ratio using direct synthesis

❖Modification of MCM-41 materials

MCM-41 materials are characterized to determine their:

❖Crystallinity - XRD

❖Textural properties (specific surface area and pore volume) - N_2 adsorption-desorption isotherm

❖Functional groups - FTIR

❖Acidity (type, density and strength) - Pyridine-FTIR, Hammett indicator

❖Thermal stability, volatile matter - TG-DTA

❖Aluminum environment in the structure - ^{27}Al MAS NMR

❖Silicon environment in the structure - ^{29}Si MAS NMR

Dibenzoylation of biphenyl, a model reaction was carried out to test the activity of the catalysts.

The properties of catalytic system will be improved in terms of

❖Acid strength

❖Amount of acid site

❖Specific surface area

Figure 1.2: Flow digram of research strategies.

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