PREPARATION OF SILICA-BASED POROUS MATERIALS FROM STARCH-DERIVED LOW MOLECULAR WEIGHT ORGANIC GELATOR TEMPLATE

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Alhamdulillah… Thanks ALLAH SWT for everything..

"..Especially for;

*My Beloved Mum***, Mesiah bt Karjan** *(1941-2009),*
This will always be dedicated to you…I really miss your presence…

My Dad, Matmin bin Kromo,
You're my hero from the day one….

My Beloved Wife, Rozita..,
Thank you for being there when everyone not..,
Many thanks for the support and understanding…

Brothers and sisters, thank you for the unconditional love…
abg jain sekeluarga, abg jai, abg zul, adi, et..Thank a lot…
Friends & families…

To all Ikhwan….
Thanks for the ukhuwwah…

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ABSTRACT

Starch, as readily available biomass source, low in cost and renewable biodegradable material, has not been paid enough attention by researchers as a promising candidate for developing sustainable materials. Starch is also referred to as a polysaccharide, mainly composed of two homopolymers of D-glucose, amylose and amylopectin building unit. The present study reports on the chemical modification of starches derived from locally-grown rice and sago to low molecular weight organic gelators (LMWOGs) for application in template-assisted synthesis of porous materials. Both rice and sago starches were modified chemically via acid hydrolysis in aqueous solutions (pH < 2) in order to break down the long branched chain of polysaccharides into much smaller monosaccharide chains of ß-D-glucose. The presence of ß-D-glucose was confirmed by Benedict's test, FTIR and NMR spectroscopy. The starch derived either from rice or sago showed similar chemical characteristics but exhibited significant differences in their granular arrangements. The rice starch granules were polygonal in shape while those of sago starch were oval shaped as revealed by FESEM micrographs. Synthesis of mesoporous silica-based materials with high surface areas (756 $m^2 g^{-1}$) were performed by employing ß-D-glucose, as organic gelator template and tetraethyl orthosilicate (TEOS) as silica precursor, in a typical HCl-catalyzed sol-gel process. The nature of interaction between silica and LMWOGs was investigated. The results show that LMWOGs act as template for the structuration of silica and the electrostatic interactions at the template-silica interface contribute to the porosity of the materials. The template removal by water as an extraction solvent and followed by calcination at 400°C were evaluated as the best template removal method. Based on the nitrogen adsorption-desorption isotherms, the pore parameters of the mesoporous silica depend primarily on the amount ratio of modified starch to silica precursor (in % v/v). At low amount of template used (< 40 % v/v) materials with micropores dominant were formed. As the template concentration is increased in medium amount ranging from 45 to 65 %v/v, the relative contribution from mesopores becomes dominant while the presence of excess amount of template resulted in low pressure hysteresis, suggesting the presence of ultramicropores. The mesoporous silica material was inserted with different titanium loadings (1, 3 and 5 wt.%) to generate titanium-silicate catalysts for the oxidation of 1-naphtol to 1,4-naphtoquinone. The catalyst containing 1 wt.% titanium which possessed the highest amount of tetrahedral titanium species as active sites exhibited the highest conversion (44 %) of 1-naphtol towards 1,4-naphtoquinone.

ABSTRAK

Kanji adalah sumber biojisim tersedia, murah dan bahan terbiodegradasi yang boleh diperbaharui, namun potensinya kurang diberi perhatian oleh penyelidik sebagai pilihan untuk membangunkan bahan mampan. Polisakarida kanji terdiri daripada dua homopolimer D-glukosa iaitu struktur kerangka unit amilosa dan amilopektin. Kajian ini melaporkan pengubsuaian kimia bagi kanji diperolehi daripada beras dan sagu tempatan sebagai "gelator organik bermolekul kecil" (LMWOGs) untuk sintesis bahan berliang dengan berbantukan templat. Kedua-dua beras dan sagu diubahsuaikan secara kimia melalui hidrolisis berasid dalam larutan akues (pH<2) bertujuan memutuskan rantaian panjang polisakarida kepada monosakarida ß-D-glukosa berantai lebih pendek. Kehadiran ß-D-glukosa telah ditentusahkan oleh ujian Benedict, spektroskopi FTIR dan NMR. Kanji yang didapati daripada beras atau sagu menunjukkan ciri kimia serupa namun berbeza dalam susunan butirannya. Kanji dari beras berbentuk poligonal manakala butiran daripada kanji sagu adalah berbentuk butiran bujur telur seperti yang dirakam dalam mikrograf FESEM. Sintesis bahan berliang meso berasaskan silika dengan luas permukaan (756 m^2 g^{-1}) dilakukan dengan menggunakan ß-D-glukosa sebagai templat "gelator organik bermolekul kecil" (LMWOGs) dan tetraetilortoslilikat (TEOS) sebagai silika prekursor dalam proses sol gel lazim bermangkin HCl. Bentuk interaksi antara silika dan LMWOGs telah dikaji. Hasil kajian mendapati bahawa LMWOGs bertindak sebagai templat untuk penstrukturan silika dan interaksi elektrostatik pada antara-muka silika dan templat menyumbang kepada sifat keliangan bahan tersebut. Penyingkiran templat menggunakan air sebagai pelarut pengekstrakkan diikuti pengkalsinan pada suhu 400°C dinilai sebagai kaedah penyingkiran templat terbaik. Berasaskan analisa isoterma penjerapan-nyahjerapan nitrogen didapati bahawa parameter liang sangat berkaitan dengan nisbah jumlah kanji terubah suai terhadap silika prekursor (TEOS) (dalam v/v %). Penggunaan templat yang sedikit (<40%) menghasilkan bahan yang mempunyai liang mikro yang dominan. Apabila penggunaan templat bertambah (dari 45%v/v hingga 65%v/v) menghasilkan liang meso yang dominan, manakala dalam kehadiran templat berlebihan histerisis bertekanan rendah berlaku kemungkinan kerana kehadiran liang ultramikro. Bahan silika berliang meso kemudiannya diselitkan dengan pelbagai muatan titanium (1 wt. %, 3 wt. %, dan 5 wt. %) secara pasca-sintesis untuk menghasilkan mangkin titanium silikat untuk pengoksidaan naphtol kepada 1,4-naphtokuinon. Mangkin dengan muatan % Ti 1 wt. yang juga mempunyai kehadiran paling banyak titanium tetrahedral menunjukkan penukaran paling banyak 44% hasil 1,4-naphtokuinon.

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LIST OF ABBREVIATIONS

2θ	Bragg angle
LMWOGs	Low molecular weight organic gelators
CuK_{α}	X-ray diffraction from copper K_{α} energy levels
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GC-MS	Gas Chromatography - Mass Spectrometry
h	hours
min	minutes
IUPAC	International Union of Pure and Applied Chemistry
nm	Nanometer
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TON	Turnover number
TOF	Turnover frequency
UV-Vis DR	Ultraviolet Visible Diffuse Reflectance
v/v	Volume/volume
wt.%	Weight percents
XRD	X-ray diffraction
λ	Wavelength

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Porous materials created by nature or by defined synthetic routes have emerged as being particularly important and have found great utility in diverse aspects of human activity. The materials are important as advanced materials for adsorption, catalysis, optoelectronic and medical applications. It is well known that the design, synthesis and modification of porous material are in a way more challenging than the synthesis of dense materials but the subject in designing, synthesis and modification of porous solids having high surface area and variable pore diameters has always fascinated scientist and remains a perpetual challenge to drive these materials to their limits.

Conventional chemicals for synthesis of porous materials such as mesoporous materials rely on fossil resources. While fossil resources is finite, biomass materials are long term solution as renewable resources for the preparation of advanced porous materials. Therefore, new strategies and techniques are constantly being developed for the synthesis and structure tailoring of nanoporous materials using locally available biomass by "templating techniques". "Templating" is commonly employed for the controlled production of materials with ordered structure having desired properties (Nidhin, 2008). Templating agents have been widely used in directing the formation of porous inorganic structures. Mesoporous materials are produced after removal of the

organic templating agents (Kresge, 1992; Sun, 2000). The study reports for the first time on the synthesis of porous silicates materials obtained from the modification of starch as organic templates and their capabilities to be used as catalytic materials.

1.2 Research Background

Effective utilization of natural renewable resources has attracted increasing attention in recent years, and become an important aspect of green chemistry (Miao *et al.,* 2008). One of the great challenges that we face in the 21st century is to build up new manufacturing industries based on renewable resources. Biomass – in the form of starch – represents a real long-term solution. From the chemists' point of view starch has many appealing properties – it is abundant and sustainable, non-hazardous, and biodegradable – properties that are becoming increasingly important in these environmentally-conscious and sustainability-driven days (Clark, 2006).

Globally, starches are major commodities in the form of derived starch; maize, cassava, sweet potato, potato and wheat. In many parts of the world, maize provides the cheapest source of starch and supplies 77 percent of global starch needs. The estimates indicate that Asia accounted for 40 percent of world starch production in the early 1990s. While nearly two thirds of world starch production was derived from maize, maize accounted for only 37 percent of starch production in Asia. In Malaysia, where the cost of cassava production is relatively high, maize appears to be the cheapest source of starch at the moment. It is found that Malaysia supply a total of 0.16 million metric tones of starch per year (Fuglie, 1998).

Previously in 2003, several groups have successfully applied natural cellulose as a template in preparation of inorganic materials (Clark, 2006). This is a significant development towards practical application of biomaterials based on the above mentioned

strategy. Native starch, as easily available, low-cost and environmentally benign biomaterials, has not been paid enough attention to advanced material synthesis, probably because starch did not possess amphiphilic charateristic as normal structures directing agents or surfactants. Therefore, there is no doubt that developing new techniques to process starch into ordered mesostructures and explore its utilization in porous material synthesis is of significance

1.3 Problem Statement

Templating agents in order to generate porous silicate materials are commonly found in the form of surfactant-type organic templates and colloidal-type templates which conventionally rely on finite fossil resources. These types of templates require tedious removal procedure and follows extreme operational work conditions. Such operational condition gives high impact towards the stability of synthesized metal oxide porous framework and affects the template reusability.

Faced with this challenge, the works report on manipulating our locally available biomass sources in the forms of polysaccharides starch derived compounds to investigate their capabilities as template in generating porous network of metal oxide. Local starches namely sago and rice are closely studied for their performance as organic templates in the process of generating silicate with pores in the mesopore range. The physiochemical properties of synthesized mesoporous silicate were also investigated.

1.4 Research Objectives

The objectives of this research are:

i. To synthesize porous silica based materials using organic templates modified starch and characterize the physicochemical properties of the obtained porous materials.

ii. To generate catalytic capabilities towards the porous silica based materials by inserting titanium transitional metal active sites to the silicate matrix surface for catalyst purposes.

1.5 Significant Output from the Research

The study is significant in utilizing our locally abundance biomass sources, in the form of polysaccharides derived starch to be used as organic templates in the synthesis of advance mesoporous metal oxide materials. The research is important in providing scientific evidence and basis for local starch to be used in more sophisticated and higher value added application.

1.6 Scope of the Study

The research covers the following scopes:

i. Study on physicochemical properties of starches from rice and sago, starches gelation and starches modification by water hydrolysis in acidic medium.

ii. Study on synthesis and characterization of porous silicate by using organic templates of hydrolyze starch.

iii. Study on incorporation and characterization of titanium transitional metal active sites into mesoporous silicate obtained from modified starches templates for oxidation catalyst.

1.7 Outline of Study

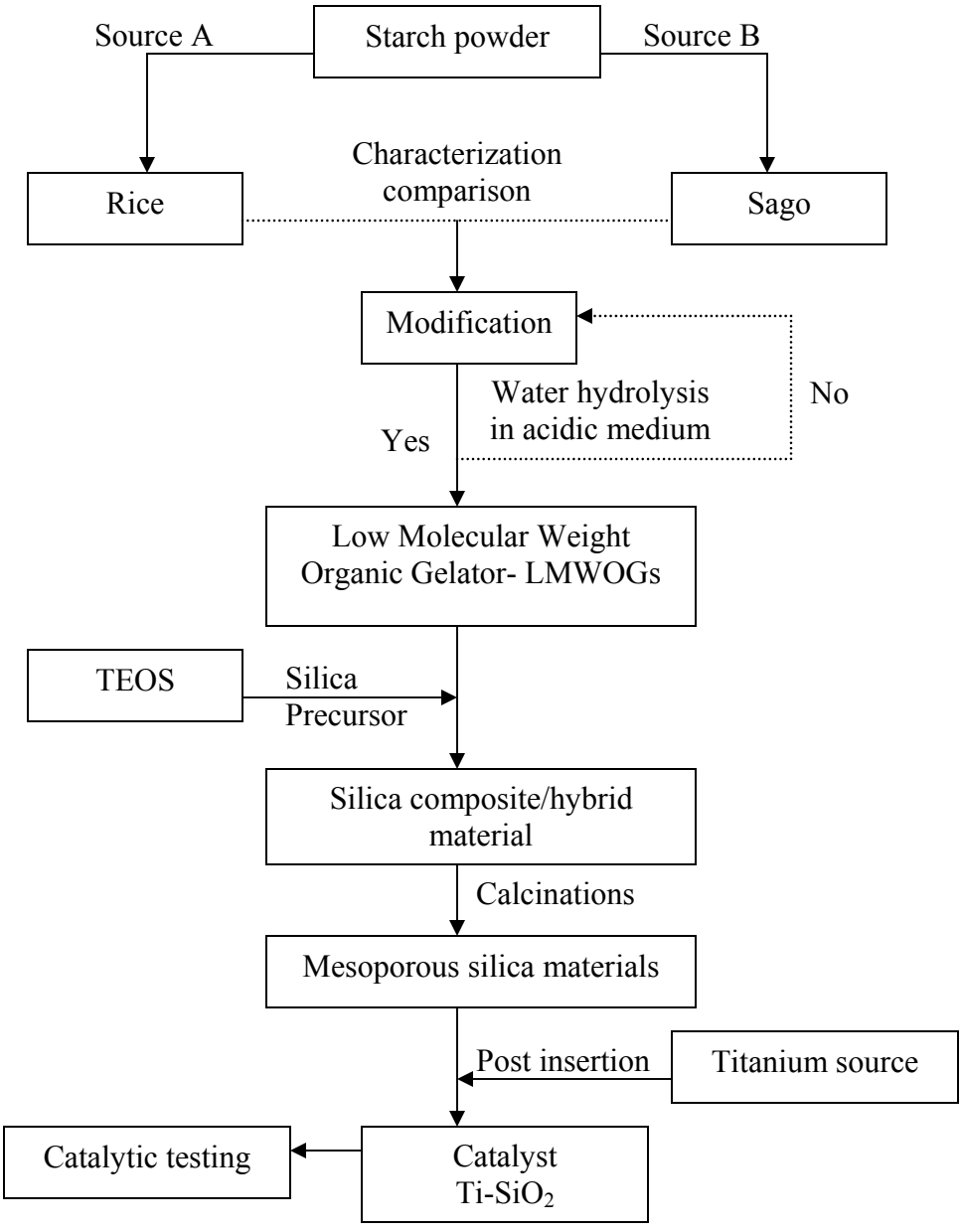

Figure 1.1: Framework outline of study.

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