Catalyst Support Made from Porous Local Clay-Fly Ash Composites for Activated Carbon Materials

by

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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2016

ACKNOWLEDGEMENT

I would like to extend my deepest gratitude to my supervisor, Dr. Mazlee Mohd Noor for giving me this opportunity to pursue my PhD under his supervision. He has constantly provided me with guidance and suggestion during my PhD study. His patience, advices, encouragement, and immersed knowledge were the main motivational factors throughout my PhD. In short, he is a good mentor to me and I would not be able to succeed my study without him.

I would also like to extend my sincere thanks to my co-supervisors, Prof. Dr. Zainal Arifin Ahmad (USM) and Assoc. Prof. Dr. Mohd Azlan Mohd Ishak (UiTM). Their knowledge has allowed me to think more creatively in solving problems when I faced with difficulties throughout my study. Although they are from different universities, they always like to share their knowledge and problem solving skills with me.

On the other hand, I would like to give an undivided gratitude to Centre of Excellence for Frontier Materials Research for the opportunity to be one of the members. Aside from Dr. Mazlee, I would like to thank Prof. Dr. Shamsul Baharin Jamaludin as the leader in the centre to provide an opportunity to be part of this group. He has also shared his knowledge and skills with me along the study in order for me to troubleshoot the problems in the study.

This research was fully funded by Malaysia Ministry of Higher Education through Fundamental Research Grant Scheme (FRGS No. 9003-00412). I would not be able to complete my study without their funding programs (MyBrain15). Therefore, I am using this opportunity to thank to Ministry of Higher Education of Malaysia for providing all these opportunities.

I would also take this opportunity to thank all my friends for the supports during my PhD study. They have given me a lot of encouragement and supports when I feel that I am not able to carry on. I am not able to go through these difficulties without their physical and mental supports.

Last but not least, I would like to thank to my parents, Mr Chan Kam Thiam and Mrs. Lim Gaik Ean for their constant encouragement and supports. I appreciate their advices in the deepest of my heart during my PhD endeavour. Their constant support has made this thesis possible.

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LIST OF ABBREVIATIONS

CFA	Porous clay-fly ash composites
CS	Conventional sintering
DEA	Diethyleneamine
DTA-TGA	Differential Thermal Analysis – Thermogravimetric Analysis
FAC	Fly ash cenospheres
FTIR	Fourier transform infrared
LOI	Loss on ignition
MAS	Microwave sintering
Ncl-PMMA	Non-crosslinked polymethylmethacrylate
PEI	Polyethyleneimine
PMMA	Polymethylmethacrylate
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinyl Chloride
SEM	Scanning electron microscope
TCP	β-tricalcium phosphate
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF SYMBOLS

Ø	Diameter
P_{total}	**Total porosity**
ρ	**Density**
σ_{b4}	**Four point bending strength**

Penyokong Pemangkin dibuat daripada Komposit Berliang Tanah Liat Tempatan – Abu Terbang untuk Bahan Karbon Teraktif

ABSTRAK

Seramik berliang telah digunakan secara meluas dalam pelbagai sektor, seperti penyokong mangkin, penukar haba, dan bahan penjerap. Daripada pelbagai teknik fabrikasi, teknik replika berasaskan busa polimer merupakan kaedah yang paling biasa dalam fabrikasi seramik berliang. Dalam penyelidikan ini, kekuatan mampatan dan lenturan komposit seramik berliang dengan nibah tanah liat-abu terbang yang berbeza (1:1 to 1:2) telah dibentangkan. Kajian ini juga menyiasat perbezaan kandungan ampaian (50 hingga 70 peratus isipadu) yang mempengaruhi sifat-sifat mekanikal dan ciri-ciri dalam pembangunan komposit seramik berliang. Komposit seramik berliang telah dibangunkan dengan menggunakan teknik replika berasaskan busa polimer. Komposit seramik berliang yang mempunyai mikrostruktur tersaling hubung menunjukkan bahawa kekuatan mampatannya boleh mencapai setinggi 1.26 MPa dengan keliangan sebanyak 94.5 peratus isipadu karbon untuk nisbah 1:1.5 antara tanah liat dengan abu terbang. Kehadiran senosfera abu terbang juga menyebabkan pembentukan lompang di dalam topang dengan ketara dan mempengaruhi sifat-sifat mampatan komposit seramik berliang. Walaupun komposit seramik berliang tersebut (nisbah 1:1.5 antara tanah liat dengan abu terbang) mempunyai kekuatan mampatan yang tinggi, namun kekuatan lenturannya hanya dapat mencapai sekadar 0.31 MPa. Ini adalah disebabkan oleh pembentukan ruang terbuka ekaarah dalam komposit seramik berliang. Selain itu, komposit seramik berliang dengan nisbah 1:2 antara tanah liat dengan abu terbang juga mempunyai kekuatan mampatan (1.12 MPa) dan kekuatan lenturan (0.79 MPa) yang bagus. Oleh sebab itu, komposit seramik berliang yang mempunyai nisbah 1:2 antara tanah liat dengan abu terbang pada 70 peratus isipadu ampaian sesuai untuk proses seterusnya dengan salutan lapisan karbon. Kandungan sukrosa (5 hingga 15 peratus isipadu) dan karbon diperolehi daripada abu terbang (0 hingga 4 peratus isipadu) yang berbeza telah digunakan untuk memahami keberkesanan lapisan karbon bersalut pada permukaan komposit berliang. Aplikasi larutan sukrosa telah bertindak sebagai pelekat dan memberi tingkah laku salingan antara karbon diperolehi daripada abu terbang dengan permukaan komposit. Sampel dengan penambahan 4 peratus isipadu karbon diperolehi daripada abu terbang mempamerkan kandungan karbon yang lebih tinggi berbanding dengan 0 peratus isipadu karbon. Ini telah menunjukkan bahawa 15 peratus isipadu sukrosa dengan 4 peratus isipadu karbon diperolehi daripada abu terbang mempunyai salutan lapisan karbon menjadi lebih baik (14.8 peratus isipadu dalam jumlah kandungan karbon). Ini sesuai untuk teruskan dengan pengaktifkan karbon. Dalam usaha untuk menentukan keberkesanan pengaktifan karbon, dua kuasa gelombang mikro berbeza yang terdiri daripada 700 W (Watt) dan 1000 W bersama dengan pelbagai tempoh pengaktifan (10 hingga 30 minit) telah digunakan. Proses pengaktifan karbon dibantu oleh kalium hidroksida (KOH) sebagai agen pengaktifan. Selepas proses pengaktifan, sebahagian besar daripada lapisan karbon terdiri daripada karbon amorfus dan grafit. Proses pengaktifan ini juga menunjukkan kuasa gelombang mikro yang tinggi (1000 W) dapat menghasilkan taburan liang mikro yang baik berbanding dengan kuasa gelombang yang lebih rendah (700 W). Oleh yang demikian, ini menunjukkan bahawa komposit seramik berliang adalah sesuai untuk digunakan sebagai penyokong mangkin untuk bahan karbon teraktif.

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ABSTRACT

Porous ceramics has been extensively applied in many sectors, such as catalyst supports, heat exchanger, and adsorbents. From various fabrication techniques, polymer sponge replica technique is the most common method in fabricating porous ceramics. In this research, the compressive and bending strength of the porous samples at different clay-fly ash ratios (1:1 to 1:2) were investigated. This study also investigated the influences of different amount of suspensions (50 to 70 wt.%) on the mechanical properties and their characteristics in developing porous ceramic composites. The porous ceramic composites were developed using polymer sponge replica technique. The interconnected microstructure of porous ceramic composites showed the compressive strength that can reach as high as 1.26 MPa with 94.5 vol.% porosity for clay-fly ash ratio of 1:1.5. The presences of fly ash cenospheres have significantly caused the formation of voids within struts and influence the compressive strength in porous ceramic composites. Although the porous ceramic composites (1:1.5 ratio between clay and fly ash) has high compressive strength (1.26 MPa), its bending strength was only able to achieve 0.31 MPa. This is attributed to the unidirectional open cell formation of the porous ceramic composites. On the other hand, porous ceramic composites with clay-fly ash ratio of 1:2 have also achieved good compressive strength (1.12 MPa) and bending strength (0.79 MPa). Therefore, the porous ceramic composites with clay-fly ash ratio of 1:2 at 70 wt. percent suspension was suitable for further process by applying a layer of carbon coating. Different amount of sucrose (5 to 15 wt.%) and fly ash-derived carbon (0 to 4 wt.%) were used in the coating process in order to understand the effectiveness of carbon coating on the surface of porous ceramic composites. The application of sucrose solution has acted as an adhesive and it provided an interlocking behaviour between the fly ash-derived carbon and the surface of porous ceramic composites. The sample with 4 wt.% of fly ash-derived carbon additions exhibited higher carbon formation as compared to 0 wt.%. This has shown that 15 wt.% sucrose with 4 wt.% fly ash-derived carbon obtained better carbon coating (14.8 wt.% total carbon content) and suitable to proceed for carbon activation. In order to determine the effectiveness of carbon activation, two microwave powers which consisted of 700 W (Watts) and 1000 W, along with various activation durations (10 to 30 minutes) were applied. The carbon activation process was assisted by potassium hydroxide (KOH) as activating agent. After activation process, the carbon layers are mainly consisted of amorphous carbon and graphite. The activation process also demonstrates that higher microwave power (1000 W) has produced better micropores distribution as compared to lower microwave power (700 W). Therefore, it has shown that porous ceramic composites are suitable to be applied as catalyst support for activated carbon materials.

CHAPTER 1

INTRODUCTION

1.1 Overview on the development of porous ceramics

In recent years, there has been a significant increase in awareness for the production of highly porous ceramic materials. This is related to the unique properties of the porous materials, including high porosity, high surface area, high thermal stability, low density and high mechanical strength (Binner, 2005). This designed porosity exhibit special features such as filtration, ion immobilization and catalyst support which cannot be achieved through conventional dense materials (Hong et al., 2012).

Typically, the uniqueness of the properties in porous ceramics has empowered them for various applications, including filtrations (Studart et al., 2007; Liu & Chen, 2014), catalyst supports (Hotz et al., 2009; Liu, 2011; Aran et al., 2012), absorption-adsorption process (Ohji & Fukushima, 2012), biomedical applications (Gonzenbach et al., 2007; Jang et al., 2014), enzyme immobilisation (Kamori et al., 2002; Mauricio et al., 2011; Datta et al., 2013), electrodes (Liu & Chen, 2014) and thermal insulation (Hong et al., 2012; Korjakins et al., 2013). Fig. 1.1 illustrates the classifications of pore size for the application of porous ceramics along with their possible fabrication techniques. In order to achieve the specific applications in porous ceramics, some of the factors have played important roles, such as cell size, morphology, and their interconnectivity (Binner, 2005). As a principle, open-cell structures are suitable to be used for catalysis activity and filtration process, whereas close-cell structures are mainly focused on thermal insulation.

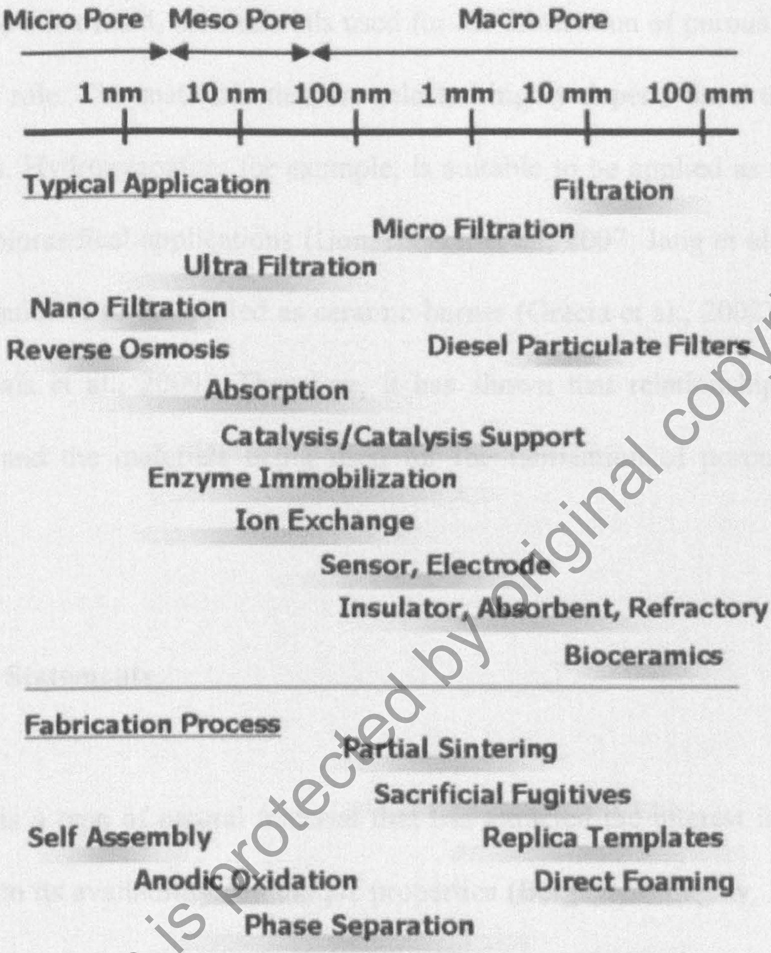

Fig. 1.1: Classification of porous materials by pore size along with typical applications and fabrication process (Ohji & Fukushima, 2012).

It is important to know that the properties of porous ceramics are related to the fabrication techniques. There is no specific technique that can sufficiently provide all the necessary structures for various applications (Sepulveda, 1997; Studart et al., 2006). Therefore, different processing route have been developed to fabricate the required properties of porous ceramics for specific applications as shown in Fig. 1.1. Basically, the fabrication techniques can generally be divided into three main categories, including polymer sponge replica technique, sacrificial template and direct foaming techniques

(Ohji & Fukushima, 2012). These processing methods mainly depend on the microstructure required in the end application along with intrinsic features of the process such as cost, adaptability and ease of fabrication (Gonzenbach et al., 2007).

On the other hand, the materials used for the fabrication of porous ceramics also play a major role. The materials that are selected highly depend upon the application environments. Hydroxyapatite, for example, is suitable to be applied as artificial bone scaffolds in biomedical applications (Gonzenbach et al., 2007; Jang et al., 2014) while cordierite is suitable to be applied as ceramic burner (Gracia et al., 2002) and filtration purpose (Ewais et al., 2009). Therefore, it has shown that relationship between the applications and the materials being used for the fabrication of porous ceramics is important.

1.2 Problem Statements

Clay is a type of natural material that has attracted the interest in studying the material due to its availability and unique properties (Bergaya & Lagaly, 2011). Clay in Malaysia is abundant and easy to obtain (Ariffin et al., 2008). However, most of the local clay has been utilised solely on conventional applications, including pottery, tiles and bricks (Noordin et al., 2012; Shakir et al., 2013; Abdullah, 2014). There are only limited studies discussed on the application of Malaysia clay for advanced applications such as biocatalyst immobilisation (Edama et al., 2013) and ceramic membrane (Ahmad & Zaidan, 2013). This shows that there is a significant potential for the clay in Malaysia to be utilised for advanced applications.

Fly ash is produced from the combustion of coal for power generation at a power plant. This means that fly ash can be considered as the environmental pollutant.

According to Balakrishnan and Awal (2014), Malaysia has generated fly ash with approximately 2 million tons every year and this figure is increasing gradually. While the environmental pollution issue increases dramatically due to fly ash exposure, researchers have taken consideration to utilise fly ash into value-added products. Maximum utilisation of fly ash has become an alternative method to reduce environmental pollution. These applications include applying fly ashes as a cement substitute in concrete (Namagga & Atadero, 2009; Islam & Islam, 2010), bricks (Xu et al., 2005; Tabin et al. 2011; Samander et al., 2013), stabiliser (Zha et al., 2008; Hakari & Puranik, 2012; Karthik et al., 2014), catalyst (Nath & Sahajwalla, 2011; Babajide et al., 2010), filler materials (Jigisha et al., 2012; Raja et al., 2013; Kar et al., 2014) and adsorbents (Chandrasekaran & Malathy, 2011; Wee, 2013; Das et al., 2015). As a result, fly ash is selected in this research as the sustainable applications.

Clay-fly ash mixtures have been widely used in construction. These applications include high performance clay-fly ash bricks (Xu et al., 2005; Pawar & Garud, 2014), backfill material for construction of reinforced bridge embankment (Jigisha et al., 2012) and liner materials (Sujit & Ambarish, 2012). However, the fabrications of clay-fly ash composites were mainly focused on developing materials with dense counterparts. There are limited studies that discussed on fabricating clay-fly ash composites in a structural matter, especially in reticulated porous structure.

The development of porous materials with a reticulated structure possessed better properties for various applications. In order to improve the properties of porous composites such as adsorption, surface modifications are required. The most common surface modification is through the coating of carbon layer (Maldonado-Hodar et al., 2008; Moreno-Callista & Perez-Cadenas, 2010; Sharanda et al., 2014). Basically, most of the carbon coating precursors is obtained from phenolic resin (Gracia-Bordeje et al., 2002; Dawson et al., 2006), furan resins (Moreno-Callista & Perez-Cadenas, 2010; Soltani et al., 2013) and furfuryl alcohol resins (Perez-Cadenas et al., 2006; Rodriguez et al., 2012). In order to obtain low cost carbon precursors, sucrose and carbon content in fly ash are the essential resources to produce activated carbon at lower cost. The carbon content in sucrose is about 30 wt.% and it also becomes adhesive after melted (Valdés-Solís et al., 2001; Jana & Ganesan, 2011). As a result, the carbon layer derived from sucrose was easily coated on the surface of structural materials. Conversely, there are only a handful of researches in using mixing carbon sources for carbon coating.

On the other hand, researchers have introduced various activation methods to produce activated carbon, including physical activation (Maroto-Valer et al., 2008; Salehin et al., 2015), chemical activation (Pengthamkeerati et al., 2010; Alhamed et al., 2015) and physiochemical activation methods (Purnomo et al., 2011; Purnomo et al., 2012). However, the longer the heating process, the higher the loss of carbon content. Microwave-assisted activation process can reduce carbon soaking at high temperature for a short period of time (Foo & Hameed, 2010; Deng et al., 2010a; Chen & Zaher, 2012; Njoku et al., 2014). As a result, microwave-assisted heating has a potential in reducing the heating period for carbon activation.

1.3 Research Objectives

The intention of this research is divided into two parts. The first part is to utilise fly ash in the porous ceramic composites fabrication. The second part is focused on fabricated porous ceramic composites acting as a catalyst support for carbon coating.

Thus, the objectives of the research are,

(i) To develop porous ceramic composites in reticulated porous structure by using local clay and fly ash.

(ii) To determine the effects of mechanical properties after the mullite and amorphous phase formation in porous ceramic composites.

(iii) To develop carbon coating on the surface of porous clay-fly ash composites.

(iv) To analyse the characteristics of carbon coating layers on porous clay-fly ash composites after activation process.

1.4 Scope of the Study

Currently, the fabrication of porous ceramic composites is still at developmental stage in Malaysia. Thus, this research has focused on the development of porous ceramics composites via polymer sponge replica technique along with the utilisation of clay and fly ash obtained in Malaysia. On the other hand, this research is divided into four sections. The first section is the testing and characterisations of the received raw materials. The second section is the mixture between clay and fly ash in a suitable mixing ratio to produce clay-fly ash composite. The composite mixture is impregnated in a reticulated structure template to form porous ceramic composites. The third section involves the extracted carbon from fly ash and sucrose as the carbon precursors. These carbon precursors are used to form a carbon coating layer on the surface of porous clay-fly ash composites. Finally, the fourth section is the activation of carbon coating layer with the assistance of chemical activating agent and microwave energy. The summary of the research works is schematically shown in Fig. 1.2.

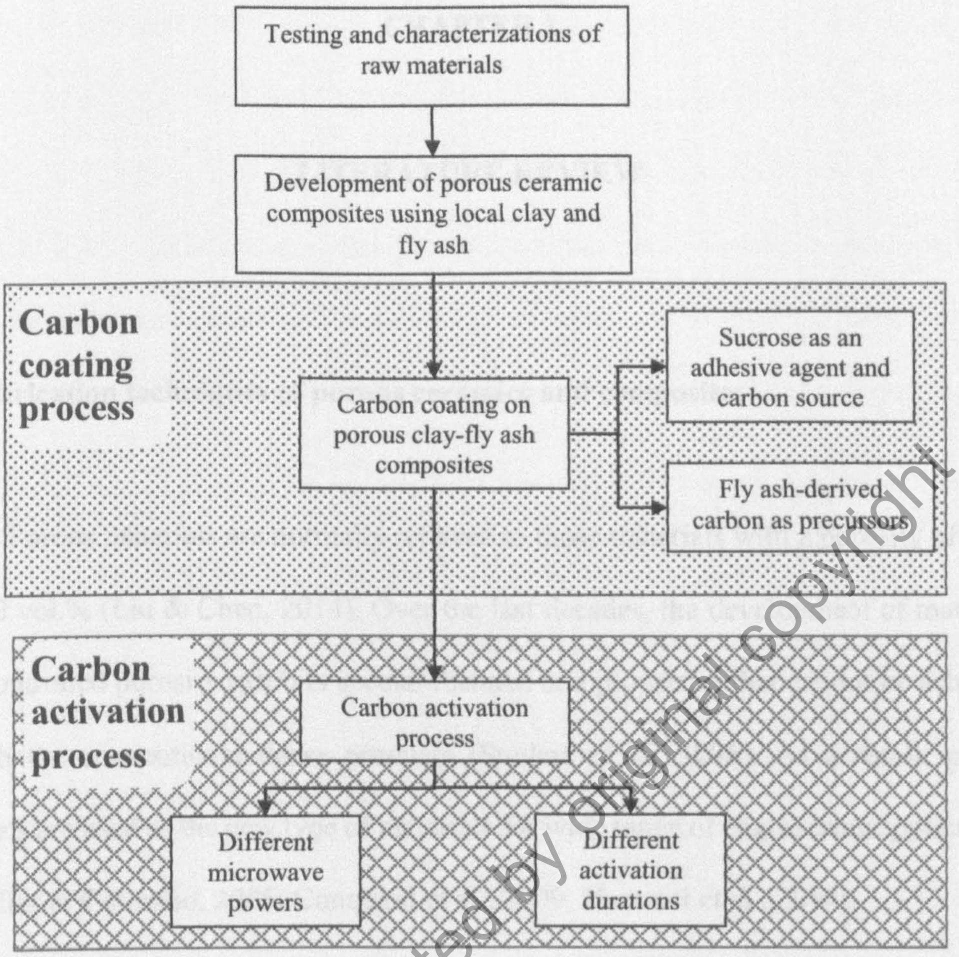

Fig. 1.2: Schematic diagram summary of the overall research work.

CHAPTER 2

LITERATURE REVIEW

2.1 Fabrication techniques of porous ceramics and composites

Porous materials are normally referred to those materials with a porosity of more than 30 vol.% (Liu & Chen, 2014). Over the last decades, the development of materials with controlled porosity exhibits special features and properties that cannot be achieved through the conventional dense products (Studart et al., 2006). As a result, porous materials are used as the new type of materials for wide range of engineering applications (Scheffler & Colombo, 2005; Conquard et al., 2009; Hammel et al., 2014).

Traditionally, the production of pores are minimised or eliminated in ceramic based materials due to their brittleness nature (Quinn & Quinn, 1997). However, the irreplaceable properties of ceramics such as high thermal and environmental stability have diversified the idea from fabricating dense solid materials to porous structure materials for various applications. These include catalyst supports and reactions (Vogt et al., 2007; Faure et al., 2011), filtration (Damoah & Zhang, 2011; Soy et al., 2011), heat exchanger (Coquard et al., 2009; Pusterla et al., 2012), thermal insulations (Liaw et al., 2011; Zhang et al., 2014a), and porous implant in biomedical applications (Chen et al., 2014; Diba et al., 2014).

The properties of porous ceramics and composites can be modified according to the specific applications through the control of their compositions and microstructures (Studart et al., 2006). The formations of open and close pores, pore size distribution,