POROUS CATALYST SUPPORT FROM CLAY – PRECIPITATED CALCIUM CARBONATE FOR CARBON NANOMATERIALS GROWTH

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by

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LIST OF ABBREVIATIONS

Al_2O_3	Alumina
Ar	Argon
ASTM	American society for testing and materials
Au	Gold
B_2O_3	Boron oxide
C_2H_2	Acetylene
$Ca(OH)_2$	Calcium hydroxide
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
$CaSiO_3$	Wollastonite
CI	Confident interval
CNMs	Carbon nanomaterials
CNTs	Carbon nanotubes
CO	Carbon monoxide
CO_2	Carbon dioxide
CVD	Chemical vapour deposition
Fe	Iron

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H_2	Hydrogen
HAP	Hydroxyapatite
K_2O	Potassium oxide
MCWNTs	Multiwalled carbon nanotubes
Mg	Magnesium
MgO	Magnesium oxide
N_2	Nitrogen
Na_2CO_3	Sodium carbonate
NaCl	Sodium chloride
NH_3	Ammonia
NH_4Cl	Ammonium chloride
PCC	Precipitated calcium carbonate
PI	Prediction interval
PPR	Paper processing residue
Pt	Platinum
P-value	Calculated probability
SEM	Scanning electron microscope
SiC	Silicon carbide
SiO_2	Quartz

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SnO_2	Tin dioxide
ß-TCP	beta-tricalcium phosphate
SWCNTs	Single walled carbon nanotubes
TGA	Thermogravimetric analysis
Ti	Titanium
TiO_2	Titanium oxide
XRD	X-ray diffraction
XRF	X-ray fluorescence
ZrO_2	Zirconia
ANOVA	One-way analysis of variance
l_o	Length of sample before sintering process, mm
l_f	Length of sample after sintering process, mm
M_1	Weight of dry sample, g
M_2	Weight of the sample after immersed in water, g
M_3	Weight of the sample after water saturated, g

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LIST OF SYMBOLS

MPa	Mega Pascal
Pa.s	Pascal.second
wt.%	Weight percent
%	Percentage
mm	millimeter
g/cm^3	Gram per centimeter cubic
rpm	Revolution per minute
R^2	Coefficient of determination

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Penyokong Pemangkin yang Berliang daripada Tanah Liat dan Kalsium Karbonat Termendak untuk Pertumbuhan Bahan Nano Karbon

ABSTRAK

Pada masa ini, bahan berliang digunakan secara meluas sebagai penyokong pemangkin, penjerapan gas, cecair, dan penderia gas. Dalam kajian ini, penyokong pemangkin diperbuat daripada campuran tanah liat dengan jumlah kalsium karbonat termendak yang dikawal iaitu 10, 15, 20, dan 25 peratus berat dengan melalui kaedah replika busa polimer. Campuran tanah liat, kalsium karbonat termendak, dan air suling dikisar dengan menggunakan 2 tempoh kisaran yang berbeza iaitu 24 dan 48 jam untuk membentuk buburan seramik. Kemudian, proses ini disambung dengan perendaman busa polimer ke dalam buburan seramik. Akhir sekali, seramik anum akan dikeringkan dan disinter pada 1250°C selama 2 jam. Objektif utama kajian ini adalah untuk mengkaji kesan penambahan kalsium karbonat termendak dan tempoh pengisaran terhadap sifat-sifat fizikal dan mekanikal penyokong pemangkin. Rangka tiga dimensi dengan struktur berliang dapat dilihat dengan jelas di dalam semua sampel. Sampel yang diperbuat daripada 25 peratus berat kalsium karbonat termendak dan masa pengisaran selama 48 jam mempunyai kekuatan mampatan yang tinggi iaitu 1.6 MPa. Selain itu, analisis varians sehala (ANOVA) menunjukkan bahawa peningkatan kalsium karbonat termendak telah meningkatkan kekuatan mekanikal penyokong pemangkin dengan pekali penentuan (R^2) adalah 0.92. Hal ini kerana kewujudan fasa baru iaitu anortit ($2CaAl_2Si_2O_8$), mulit ($3Al_2O_3 \cdot 2SiO_2$) dan gehlenit ($3Ca_2Al_2SiO_7$). Selain itu, ketumpatan busa meningkat apabila peratus keliangan menurun. Ketumpatan busa untuk sampel yang diperbuat daripada 25 peratus berat untuk tempoh pengisaran 48 jam adalah lebih tinggi (1.05 g/cm^3) berbanding sampel yang lain. Sebaliknya, peratus keliangan menurun (55 peratus) apabila jumlah kalsium karbonat termendak dan tempoh pengisaran meningkat. Di samping itu, ketumpatan ketara (2.79 g/cm^3) adalah hampir sama dengan ketumpatan teori untuk seramik anorthit iaitu 2.76 g/cm^3. Hubungan antara kekuatan mekanikal terhadap peratus keliangan adalah negatif, di mana kekuatan mekanikal akan meningkat apabila peratus keliangan menurun. Sampel yang dikisar selama 48 jam menunjukkan sekaitan yang tinggi dengan pekali penentuan (R^2) sebanyak 0.91. Manakala, hubungan antara kekuatan lenturan dan kekuatan mampatan terhadap ketumpatan busa adalah positif, dimana kekuatan mekanikal akan menurun apabila ketumpatan busa menurun. Sampel yang dikisar selama 48 jam menunjukkan sekaitan yang kuat dengan pekali penentuan (R^2) sebanyak 0.81. Oleh yang demikian, sampel yang diperbuat daripada 25 peratus berat komposisi kalsium karbonat termendak dan dikisar selama 48 jam adalah sampel yang paling sesuai digunakan sebagai penyokong pemangkin untuk pertumbuhan bahan nano karbon kerana mempunyai kekuatan mekanikal yang diperlukan. Bahan nano karbon telah di sintesis di atas permukaan penyokong pemangkin melalui kaedah pemendapan wap kimia. Ferosena dan aseton telah digunakan sebagai pemangkin dan sumber karbon. Suhu yang digunakan untuk proses ini adalah 750°C selama 30 minit. Bahan nano karbon adalah dalam bentuk kusut serta bergulung dan dapat dilihat di sepanjang topang penyokong pemangkin.

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Porous Catalyst Support from Clay – Precipitated Calcium Carbonate for Carbon Nanomaterials Growth

ABSTRACT

Currently, porous materials were widely used as catalyst supports, adsorption of gases or liquid, and gas sensors. In this research, the fabrication of catalyst support utilised clay with controlled amounts of precipitated calcium carbonate (PCC) at 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.% via a polymeric foam replication method. A mixture of clay, precipitated calcium carbonate, and distilled water were ball milled for 24 hours and 48 hours milling durations in order to form ceramic slurries. After the impregnation process of polymeric foam into ceramic slurries, the green ceramic was dried and sintered at 1250°C for 2 hours holding time. The main objectives of this research are to study the effects of precipitated calcium carbonate additions and different milling durations on the physical and mechanical properties of the catalyst support. The sample that was fabricated with 25 wt.% of precipitated calcium carbonate and milled at 48 hours was found to have the highest compressive strength which at 1.6 MPa. Besides, one-way analysis of variance (ANOVA) showed that the increase between 10 wt.% and 25 wt.% of PCC has significantly increased the strength of the catalyst support and the coefficient of determination (R^2) at 0.92. The increase of the mechanical strength was attributed to the transformation of new phases such as anorthite ($2CaAl_2Si_2O_8$), mullite ($3Al_2O_3{\cdot}2SiO_2$), and gehlenite ($3Ca_2Al_2SiO_7$). On the other hand, foam density would increase when the percentage of porosity decreased. The sample that was fabricated with 25 wt.% of PCC and milling for 48 hours has the highest foam density (1.05 g/m^3) compared to other samples. In contrast to the percentage of porosity, the porosity decreased to 55 percent after the amount of PCC and milling duration increased. The apparent density (2.79 g/cm^{3-}) was approximately similar with the theoretical density (2.76 g/cm^3) of the anorthite ceramics. The correlations between the flexural and compressive strength on the porosity of the catalyst support have shown negative correlations where the mechanical strength would increase when the porosity decreased. Samples with 48 hours milling duration have shown a strong correlation with a coefficient of determination (R^2) of 0.91. The correlation between the flexural and compressive strength on the foam density of the catalyst support has shown a positive correlation where the mechanical strength would decrease when the foam density decreased. Samples with 48 hours milling duration have shown a strong correlation with the (R^2) of 0.81. Thus, the sample that was fabricated with 25 wt.% of PCC and ball milled for 48 hours was suitable for the application of catalyst support for the growth of carbon nanomaterials (CNMs) because it has higher mechanical strength. The CNMs were grown on the surface of the catalyst support via a chemical vapour deposition method at 750°C for 30 minutes reaction time. The ferrocene and acetone were used as a catalyst and carbon source, respectively. The tangled and curled carbon nanomaterials were observed along the strut of the catalyst support.

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CHAPTER 1

INTRODUCTION

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1.1 Research background

Catalysts such as gold (Au), iron (Fe) and platinum (Pt) are substances or materials that can be used to improve or increase the reaction rate in the specific process such as oxidation, gas and liquid adsorption processes (Hakeem et al., 2016; Rey et al., 2016; Wang et al., 2016a). The performance of the catalyst can be enhanced by placing the catalyst on solid support also known as catalyst support. Porous ceramic are the most promising materials for catalyst support owing to their high porosity, high specific surface area, good thermal properties, high chemical stability and high mechanical strength (Antolini & Gonzalez, 2009; Kaiser et al., 2016; Mehr et al., 2016). As a consequence, numerous types of ceramic catalyst supports such as mesoporous silica and alumina catalyst supports have been developed (Li et al., 2010; Khosravi et al., 2016; Hu et al., 2016).

Several methods have been used to develop porous ceramic such as slip casting (Han & Shu, 2016), extrusion (Fiocco et al., 2016), foaming (Li & Liang, 2015), and replication methods (Gonzalez et al., 2016). In this research, the fabrication of catalyst support utilised clay and PCC via a polymeric foam replication method. Generally, the fabrication of the porous material using this method can produce porosity in the range of

40% to 95% (Kocakusakoglu et al., 2015). International Union of Pure and Applied Chemistry (IUPAC) categorises pore diameter (*d*) into 3 sections, namely microporous (*d* smaller than 2 nm), mesoporous (*d* between 2 nm and 50 nm) and macroporous (*d* larger than 50 nm) (Costacurta et al., 2007).

Clay such as flint clay, china clay and ball clay has received widespread attention in the fabrication of ceramic since 5000 B.C. due to its availability and unique properties (Fahrenholtz, 2008). The properties of clay minerals such as hardening after sintering or firing process made the fired clay being widely used in structural building, and adsorption applications. Besides, clay minerals are also categorised as non-polluting materials and are currently used as depolluting agent (Louhichi et al., 2016). Precipitated calcium carbonate (PCC) is a synthesised calcium carbonate and has high purity of calcium with low particle size. Commonly, the PCC is synthesised from the limestone and waste materials that contains high percentage of calcium (Price et al., 2011).

Carbon nanomaterials (CNMs) have been widely used as hydrogen storage, coating material to increase corrosion resistance and carbon dioxide (CO_2) adsorbent due to the unique physical and mechanical properties (Heer, 2002; Ngoy et al., 2014). Basically, CNMs are divided into various types such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) (Guang et al., 2005). Various methods such as chemical vapour deposition (CVD), arc discharge, laser ablation, and electrolysis have been used to synthesise the CNMs (Paradise & Goswami, 2007). In this research, the CVD method was used to synthesise the CNMs. In fact, CVD method can produce high scale and high purity of CNMs (Su et al., 2000; Hoecker et al., 2016).

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1.2 Problem statements

i. The addition of calcium carbonate ($CaCO_3$) such as limestone, chalk, and waste material into the clay minerals can enhance the physical and mechanical properties of the ceramic. However, the addition of the calcium carbonate into the clay minerals has a limit (Ewelina & Ma, 2013). Sutcu and Akkurt (2010) utilised paper processing residues (PPR) as a calcium carbonate source for the fabrication of anorthite ceramics. PPR contains only 32.91 wt.% of calcium oxide (CaO). They have found that the compressive strength of the ceramic decreased after the PPR was increased to 40 wt.%. The increasing of the impurities in the PPR has led to the decrease of the mechanical strength of ceramic. Thus, it is necessary to study the effects of various additions of high purity of calcium carbonate such as PCC on the physical and mechanical properties of the catalyst support.

ii. The milling process in the fabrication of ceramic is very crucial in the homogeneity of two or more different particles (Lee & Iqbal, 2001). Furthermore, the reduction of the particle sizes has improved the performance of the sintering process and led to the improvement in the physical and mechanical properties of ceramic (Fang et al., 2009). Hence, it is important to study the effects of different milling durations on the physical and mechanical properties of the catalyst support.

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iii. The growth of CNMs on the porous metal substrate was extensively studied by researchers. Previously, the researchers utilised graphene and stainless steel foam as porous metal substrates to grow CNMs (Liu et al., 2014; Latorre et al., 2016). However, the fabrication of porous metal substrates were expensive compared to the fabrication of porous ceramic substrate. On the other hand, the studies in the growth of CNMs on porous ceramic substrates such as alumina and mesoporous silica were limited (Mazumder et al., 2016). Therefore, it is necessary to evaluate the growth of CNMs on the porous ceramic.

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1.3 Objectives

The present study is mainly to develop a catalyst support for CNMs growth. The primary objectives of this project are divided into the following categories:

i. To fabricate a catalyst support from clay and controlled amounts of PCC via a polymeric foam replication method.

ii. To analyse the physical and mechanical properties of the catalyst support at various amounts of PCC and different milling durations.

iii. To investigate the correlation of mechanical strength over the percentage of porosity and foam density of the catalyst support via statistical analysis.

iv. To evaluate the feasibility of the growth of CNMs on the porous ceramic.

1.4 Scope of study

The first phase of this study began with characterised the chemical composition, mineralogical phase, microstructural analysis and weight losses of raw materials. Then, the process was followed by the fabrication of the catalyst support via a polymeric foam replication method.

At the second phase the physical and mechanical properties of the catalyst support was characterised and tested. The chemical composition, mineralogical phase, physical characteristics such as density, porosity, and percentage of linear shrinkage of the catalyst support was investigated. Then, the mechanical properties of ceramic foam were analysed using compression and four-point flexural test. Then, the correlations between the physical properties and the mechanical properties of the catalyst support was evaluated using statistical analysis.

The third phase of this study continued with the modification of the catalyst support surface. The catalyst support was coated with CNMs and the CNMs was later synthesised using CVD method.

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CHAPTER 2

LITERATURE REVIEW

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2.1 An overview of porous ceramic

Porous ceramic are commonly used as catalyst supports (Thompson et al., 2013; Zhu et al., 2013; Mendes et al., 2016), thermal insulators (Fukushima & Yoshizawa, 2014), gas or liquid separations (Moreira et al., 2004), and heat exchangers (Yin et al., 2016) due to their outstanding properties namely, high specific surface area, high porosity, low density, and high temperature resistance. The main purposes of fabricating the ceramic material are to enhance the physical and mechanical properties of the materials (Rezwan et al., 2006).

Kim et al. (2016) prepared porous mullite-based ceramic by utilising coal fly ash and Al_2O_3 powder via a freeze casting method and was sintered at a temperature between 1300°C to 1500°C. The compressive strength increased with the increase of sintering temperature. However, the compressive strength of the porous mullite-based ceramic would decrease from 33.1 MPa to 8.1 MPa when the porosity increase from 51.4% to 78.9%. It can be deduced that the mechanical and physical properties of porous ceramic were influenced by various parameters such as sintering temperatures and percentage of porosity. On the other hand, the fabrication methods also gave an impact to the properties of the porous ceramic.