EFFECT OF DIFFERENT BINDER ON THE FABRICATION OF POROUS CORDIERITE

by

NURUL SYAZWANI BINTI OTHMAN

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DECLARATION

I declare that this thesis is the result of my own research, does not incorporate without acknowledgement any material submitted for the degree or diploma in any university and does not contain any materials previously published, written or produced by another person except where due references are made in the text.

Signature :

Candidate's Name : Nurul Syazwani Binti Othman

Date :

Signature :

Supervisor's Name : Associate Professor Dr. Hasmaliza Mohamad

Date :

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Nurul Syazwani Bt Othman

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LIST OF ABBREVIATION

ASTM	The American Society for Testing and Materials Standard
DPF	Diesel Particulate Filter
IUPAC	International Union of Pure and Applied Chemistry
PAAm	poly (acrylamide)
ppi	pores per inch
PVA	Polyvinyl Alcohol
SEM	Scanning Electron Microscope
TGA	Thermal Gravimetric Analysis
XRD	X-Ray Diffraction

KESAN PERBEZAAN PENGIKAT KE ATAS PEMBENTUKAN KORDERIT BERLIANG

ABSTRAK

Korderit berliang telah difabrikasi melalui kaedah replikasi span polimer. Magnesium oksida (MgO), aluminium oksida (Al_2O_3) dan silikon dioksida (SiO_2) digunakan sebagai bahan mentah dengan penambahan pelbagai jenis pengikat yang berbeza. Pengikat-pengikat yang digunakan adalah kanji sagu, kanji ubi kayu dan polivinil alkohol (PVA). Kajian ini memberi tumpuan kepada kesan penambahan pelbagai pengikat dengan peratusan pengikat yang berbeza (0 wt%, 3 wt%, 5wt%, 8 wt% dan 10wt%) dalam penghasilan korderit berliang menggunakan komposisi stoikiometri korderit ($2MgO.2Al_2O_3.5SiO_2$). Replika span dicelup dengan buburan bahan mentah korderit dan dikeringkan (80 °C selama 24 jam) sebelum di sinter pada suhu 1350 °C selama 2 jam. Analisis terma gravimetrik (TGA) telah dilakukan untuk mengenalpasti suhu pelesapan pengikat-pengikat dan replika span. Kelikatan buburan diukur dengan menggunakan viskometer. Ketumpatan dan keliangan diperolehi menggunakan kaedah Archimedes. Morfologi sampel yang disinter diuji dengan mikroskop imbasan elekton (SEM) dan kekuatan mampatan diperolehi dengan ujian mampatan. Pencirian dilakukan untuk mengenalpasti ketulenan korderit melalui pembelauan sinar-X (XRD). Keputusan XRD menunjukkan bahawa sampel yang terhasil adalah korderit tulen tanpa kehadiran bendasing. Analisis kelikatan menunjukkan bahawa, semua buburan dengan penambahan pengikat mempunyai kelakuan aliran pseudoplastik. Korderit berliang menghasilkan sel terbuka dengan rangka yang berhubung, kurang keretakan pada rangka dan mempunyai rangka yang jelas disebabkan oleh salutan buburan yang tebal. Julat keliangan korderit berliang dengan penambahan sagu, ubi kayu dan PVA ialah 85-92%, 84-89.5% dan 82-88.9%, masing-masing. Julat kekuatan mampatan yang diperoleh ialah 0.23-0.29 MPa, 0.20-0.33 MPa dan 0.25-0.39 MPa, masing-masing. Pengikat bukan sahaja membantu proses pembentukan dan memberi kekuatan, malah bertindak sebagai agen pembentuk liang. Keputusan yang diperoleh dari kajian menunjukkan bahawa penambahan pengikat yang berbeza mempengaruhi sifat-sifat korderit berliang yang telah dihasilkan.

EFFECT OF DIFFERENT BINDER ON THE FABRICATION OF POROUS CORDIERITE

ABSTRACT

Porous cordierite was fabricated by using replication sponge method. Magnesium oxide (MgO), aluminium oxide (Al_2O_3) and silicon dioxide (SiO_2) were used as raw material with addition of different types of binder. The binders used were sago starch, tapioca starch and polyvinyl alcohol (PVA). This study was focus on the effect of various binder addition with different percentage of binder used (0 wt%, 3 wt%, 5wt%, 8 wt% and 10wt%) in the production of porous cordierite using stoichiometric of cordierite ($2MgO.2Al_2O_3.5SiO_2$). The sponge was impregnate into the feedstock of cordierite slurry and dried (80 °C for 24 hours) prior sintered at temperature 1350 °C for 2 hours. Thermal Gravimetric Analysis (TGA) was done to determine the burnt out temperature of binders and sponge. The viscosity of slurry was measured using viscometer. Density and porosity were obtained by using Archimedes method. Morphology of sintered sample was studied using Scanning Electron Microscope (SEM) and the compressive strength was obtained from compressive test. Characterization was done to observe the purity of cordierite through X-ray diffraction (XRD). XRD results show that, the samples produced were pure cordierite without presenting impurity. Viscosity analysis shows that, all the slurries added with binder have pseudoplastic flow behavior. Porous cordierite creates open cell with the interconnected skeleton, less fracture skeleton and well-defined skeleton causes from the thicker coating of slurry. Range of porosity obtained with addition of sago, tapioca and PVA were 85-92%, 84-89.5% and 82-88.9%, respectively. Range of compressive strength obtained were 0.23-0.29 MPa, 0.20-0.33 MPa and 0.25-0.39 MPa, respectively. Binder was not only assists in formation process and give strength, but also acts as pore forming agents. Results obtained from the study shows that the addition of different binder affects the properties of porous cordierite produced.

CHAPTER 1

INTRODUCTION

1.1 Porous Cordierite

Cordierite with composition $2MgO.2Al_2O_3.5SiO_2$ is one of the most interesting phases in the ternary system of magnesium-aluminium-silicate, $MgO-Al_2O_3-SiO_2$ (MAS). It could exhibit very low thermal expansion over a whole range of temperature and thus, offers outstanding resistance to the thermal shocks in case of an abrupt temperature change (Albhilil et al., 2013). Besides, cordierite has low dielectric constant and high chemical and mechanical durability. Ceramics materials based on cordierite, therefore, are widely used as honeycomb-shaped catalyst carriers in automobile exhaust systems, as substrate material for integrated circuit boards and as refractory materials (Naskar et al., 2004).

In the form of structural porous ceramics materials, a very wide application has been encourages due to the unique structure which given several properties such as low density, high porosity, low thermal conductivity, high specific surface area, high permeability and high temperature resistance. The properties of porous ceramic influenced by their structure and the relatively poor mechanical properties are attributed to processing-related flaws (Colombo, 2002). These types of ceramic has potential to be used in various industrial fields such as inorganic membrane reactor (Julbe et al., 2001), filters (Ewais et al., 2009), porous medium burner for gas and liquid combustion (Ismail et al., 2013), thermal barrier (Cernuschi et al., 2004), ceramic-metal composite perform (Mattern et al., 2004) and also electrical power generation through thermo-photovoltaic system (Qiu et al., 2007). The development of porous ceramics was dependent on the fabrication method.

1.2 Methods to Produce Porous Cordierite

The manufacturer of porous ceramic has become a famous and considerable interest in recent years because of wide used in applications. There are many types of porous ceramic are currently developed from different kinds of materials and types of processing routes. Colombo (2006) and Studart et al. (2006) has defined a number of processing routes for the fabrication of porous ceramic.

The methods generally are classified into three categories: replication method, direct foaming and sacrificial template method. Ewais et al. (2009) were studied the method of replication by using a mixture composed of waste silica fumes, bauxite and talc, while, Fukushima et al. (2008), prepared porous cordierite by gelation and freezing method. Eftekhari et al. (2007) obtained cordierite powder from kaolin, ball clay, talc, magnesite and aluminium hydroxide, and fabricated the porous bulk cordierite using cordierite powder as material. Alves et al. (1998) fabricate porous cordierite using starch consolidation and Jang et al. (2007) fabricated porous cordierite ceramics from talc and alumina filled polysiloxane using expandable microspheres as pore former.

1.3 Problem Statement

In the porous ceramic applications, the fundamental properties of these materials such as mechanical behavior, bulk density, apparent porosity, needs to be considered for the design purposes. The relationship between properties and the microstructure of porous ceramics becomes important factors which were affected to the performance of porous ceramics. There needs to understand in fact, the properties of porous ceramics was closely related to their relative density as well as the morphology, size and distribution of the holes. All of these features were highly influenced by the processing routes used to fabricate the porous materials. Replication technique is considered to be the most popular processing routes which involve the impregnation of a natural or synthetic sponge with ceramic slurry. During fabrication, ceramic slurry was coated and adheres to the surfaces of the sponge skeletal, subsequently sintering process promotes burnt out of the sponge and leaving behind a porous ceramic structure imitated the original template (Studart et al., 2006). However, the space occupied by the polymer remains as an internal defect in the ceramic body and sometimes, the thin layer of ceramic slurry coated on the substrate resulted to very thin walls between the pores and thus, causes the porous ceramics to have low strength (Thijs et al., 2003).

In order to improve the properties of porous ceramics, additives were used to gives better formation. Apart from this, the used of binder in the development of porous ceramic are investigated since it serve the primary function of providing strength by building bridges between the particles. Oliveira et al. (2005) fabricate porous cordierite using replication method, from the powder mixture materials (ball clays, talc, alumina and silica) with addition of dispersant agent and different percentage of sodium bentonite (0 wt%, 3 wt% and 5 wt%, respectively). However, since sodium bentonite was categorized as nonorganic materials, thus, this would interfere the cordierite phases.

There are various types of organic binder used in the preparation of porous ceramics. Natural binders such as potato, corn, tapioca and wheat has been used as a thermoplastics starch since they were primary sources of environmentally friendly materials, cheap, abundant and easy to handle and process (Trovati et al., 2010). The other polymer binder used was synthetic binder such as polyvinyl alcohol (PVA) polyethylene glycol (PEG) (Taktak et al., 2011). Recently, Jamaludin et al. (2014) fabricate porous porcelain using sago as binder and pore forming agent. With addition of sago starch as binder consequently the construction of smooth coating surface on the porous porcelain. Han et al. (2003) combined the replication technique with pore-former method by using polyvinyl alcohol (PVA) as binder and pore former material. The sponge template will provide open cell structure within millimeter range, whilst the binder created micro-pores. Thus, the used of organic binder would helped better formation of porous cordierite.

Despite of being considered as an ideal material for varies application, synthetic and natural materials based on magnesium, aluminium and silicon dioxides were employed to produce cordierite (Kobayashi et al., 2000; Goren et al., 2006). Talc, china clay, kaolin, magnesite and quartz are usual natural materials used to produce cordierite ceramics which could help the sintering process. However, due to the fact that those natural mineral were not abundant and pure enough, thus, cordierite have to be synthesized from the ternary phase diagram $MgO-Al_2O_3-SiO_2$ (Albhilil, 2013). The used of high purity raw materials, which mixed in amounts conforming to the theoretical composition of cordierite will produced the product with lowest thermal expansion coefficient and high resistance to the thermal shock.

Therefore, in this study, the fabrication of porous cordierite using replication method combining with pore former method was chosen. Purely oxide materials (MgO,Al_2O_3 and SiO_2) will be used. In this approach, organic binders were used since it does not only provide strength but also act as pore former agents in order to increase the porosity value. The addition of binder enhanced the rheological of ceramic slurry which later influenced the properties of porous cordierite. The rheological behavior of cordierite suspensions at different shear rate were studied in order to obtain good workability as the fluid have enough to penetrate into the sponge under shear. In this work, sago starch, tapioca starch and polyvinyl alcohol (PVA), were added as a binder to enhance the coating process on the sponge template. The amount of each binder was varied (0 wt%, 3 wt%, 5 wt%, 8 wt% and 10 wt% respectively). The sponge template was then impregnated with the ceramic slurry prior to drying and sintering. The characterization of porous cordierite such as density, porosity and compressive strength was done to observe the properties obtained using different types of binders.

1.3 Research Objectives

This study is concentrating on synthesize and characterize of porous cordierite by polymeric sponge replication technique, using mainly pure oxide materials with addition of different types of binder. Thus, the objectives are:

i) To produce porous cordierite from pure oxide materials

ii) To observe the effect of different binders (sago starch, tapioca starch and polyvinyl alcohol) in production of porous cordierite

iii) To find the optimum percentage of all binder possible to be used in fabricate the porous cordierite.

1.4 Scope of Research

In this research, porous cordierite was fabricated by using oxide materials (MgO, Al_2O_3 and SiO_2) as the main raw materials with addition of different type of binder. There are sago starch, tapioca starch and polyvinyl alcohol (PVA). The compositions used to fabricate porous cordierite were according to the stoichiometric of cordierite ($2MgO.2Al_2O_3.5SiO_2$) in the ternary system. This study involves the characterization of raw materials and binders, the fabrication of porous cordierite, the rheological flow behavior of cordierite ceramic slurry and characterization of the porous cordierite such as density, porosity, SEM morphology and compressive strength.

CHAPTER 2

LITERATURE REVIEW

2.1 Porous Ceramics

Porous ceramics contain high porosity materials is actually exhibit special properties and was used in wide range of technological applications (Studart et al, 2006). Figure 2.1 shows the example of porous ceramics. The pores generated were not become a problem since a huge number of applications appeared especially for environments where high temperature are involved. Materials with controlled porosity have already exhibited special features and properties which cannot be fulfilled by their conventional dense counterparts.

Figure 2.1 Some examples of porous ceramics (Lucacci 2010)

Porous ceramics were investigated since its exhibit a rather unique combination properties such as low density, low thermal conductivity, high porosity, high specific surface area and others, making them indispensable for various engineering applications (Green and Colombo, 2003). These characteristics are essential for various applications but depends on their nature and structure (either open or closed cells), which include:

filtration of molten metals or particulate from exhaust gases, radiant burners, catalyst supports, biomedical devices, kiln furniture, reinforcement for metal or polymer matrix composites, bioreactors and heat exchangers (Scheffler & Colombo, 2005). All of the applications require porous component to possess a specific range of value for different properties that can be achieved by selecting appropriate fabrication method (Sepulveda, 2000).

The properties of each specific application can be achieved by controlling the composition and microstructure of the porous ceramic. The criteria of open or closed pores porosity, pore size distributions and pore morphology influences the material properties (Studart et al., 2006). In order to get those properties, they are hugely influenced by the processing routes for the production of porous ceramics. It can be produced using several methods. The most widespread processing approach for open-cell porous ceramic is to coat open pores polymer foams with a ceramic powder dispersed in a liquid or also known as slurry which was patented by Schwartzwalder and Somer in 1963.

Porous ceramics can be categorized as open or closed pores. Figure 2.2 shows the image of foams. Both types consist of an assembly of irregularly shaped polyhedral cells enclosed by three dimensional strut network. For the open pores, the pores are connected to each other with solid edges (strut) and pores to pores connectivity takes place via open faces (windows), whereas, in closed-cell foams, the pores are connected to each other with solid faces with no interconnectivity between them (Scheffler & Colombo, 2005).

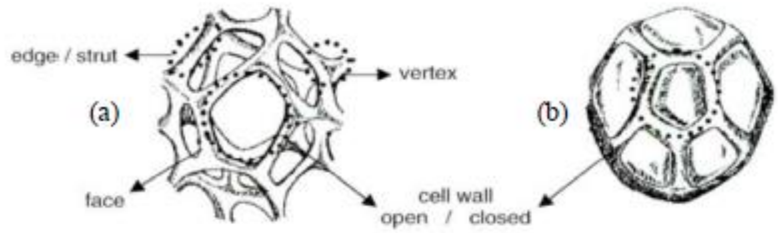

Figure 2.2 Components of the structure of a cell unit in a) open pores foams b) closed pores foams (Scheffler & Colombo, 2005)

2.1.1 Classification of Porosity

Materials containing voids and porosity are classified into three types depending on the open pore diameter, d: macro-porous (d > 50 nm), meso-porous (50 nm > d > 2 nm), and micro-porous (d < 2 nm), according to the nomenclature of IUPAC (International Union of Pure and Applied Chemistry) (Ohji and Fukushima, 2012; Ohji, 2013). The classifications of cellular material are made in reference to the typical application of the respective size of cell and pore. Currently, the widespread applications for porous material have instigated many processing method in order to accommodate the requirement of smaller pore size into the nanometer range. One of the most known and suitable application of porous ceramic is the filtration or separation of matters in fluids. Filtration is roughly classified into several classes depending on pore diameter, d, and molecular weight cut-off of the matters (MWCO) where, filtration (typically d > 10 mm), microfiltration (10 mm > d > 100 nm), ultrafiltration (100 nm > d > 1 nm,), nanofiltration (~1-2 nm), and reverse osmosis (d < 1 nm).

2.1.2 Types of Porous Ceramic

Porous ceramic can be produced from different types of materials such as alumina (Khattab et al., 2012), porcelain (García-Ten et. al., 2012), mullite (Yang et al., 2012), silicon carbide (SiC) (Dey et al., 2011), cordierite (Fukushima et al., 2008) and others. Most of the materials are experienced in the fabrication of porous ceramic by replication polymeric sponge. Porous alumina is the most popular material candidate owing to the high melting point (2050°C), low thermal coefficient of thermal expansion (CTE), inertness to water and chemical attack, high strength attack, high strength, ease of processing and abundant in nature various researcher have study the usage of alumina to produce cellular structure using different method and technique. Via the replication polymeric sponge, porous alumina resulted with well-defined cell size, however, the products suffers low mechanical strength since the presence of hollow strut (Luyten et al., 2009; Peng, et al.,2000). Han et al. (2003) combined the replication technique with pore former method by using polyvinyl alcohol (PVA) as binder and pore former material. The sponge template will provide open cell structure within range, whilst the binder created micro-pores.

Porous silicon carbide (SiC) also promotes excellent properties in the wide range of industrial applications using different fabrication methods. In the manufacturing of sponge replication technique, Soy et al. (2011) fabricate porous SiC by using bentonite as the sintering additives to achieved good properties. With the mixture of SiC, the bentonite was functioning well as binder for the ceramic slurry. An increased of bentonite addition to 10% resultant in higher strength for the porous ceramic. At the same times, when the SiC loading in the slurry increased, it contribute to the increasing strength of porous SiC.

Mullite also has reputation as an outstanding as material in the production of porous materials. Roncari et al. (2000) has studied the dispersing behavior of MgO-doped mullite suspension via the fabrication of reticulated ceramics by sponge impregnation technique. The optimum dispersing conditions and different defflucculant agents was found and reticulated mullite samples were produced successfully. There many available methods to fabricate porous mullite and other ceramics material as well. Sacrificial template, gel-freeze drying, simple partial sintering technique and other combination of several techniques is the processing route had in the porous ceramics manufacturing.

2.2 Cordierite and Porous Cordierite

Cordierite is a magnesium-aluminium-silicate mineral. It can be an attractive ceramic materials and important phases of the $MgO\text{-}Al_2O_3\text{-}SiO_2$ system due to many industrial applications. Cordierite was known and used as a gemstone in Sri Lanka long before the French geologist mineralogist Pierre LoiusCordier accurately described it in 1809. It was identified as specific mineral and named in 1813 (Chowdhury et al., 2007). Generally, cordierite has stoichiometric formula of $2MgO.2Al_2O_3.5SiO_2$. The excellent properties of cordierite, such as very low CTE, low density, and good thermal shock resistance have made it a promising candidate for advanced applications (Schneider et al., 2008; Yamuna 2004). Due to these properties, the cordierite have been used for example, as a kiln furniture, carriers of purifying exhaust emission, filter for liquid at high temperature, glaze for tiles and partial electronic component (Shi et al., 2001). With regard to the large field of application in industrial area, synthetic and natural materials based on magnesium, aluminium and silicon oxides were employed to produce cordierite ceramics (Goren et al., 2006; Kobayashi et al., 2000).

Figure 2.3 shows the phase diagram or ternary system of magnesium-aluminium-silicate in order to determine the composition and temperature necessary for the cordierite phases. While, Table 2.1 shows the general properties of cordierite (Bertoldi et al., 2004). Cordierite exists in three polymorphic forms. There are α-Cordierite, β-cordierite and μ-cordierite (Goren et al., 2006a). α-Cordierite is the only phase that can be obtained by solid-state reaction from oxides precursor. The stable forms are that of hexagonal symmetry (α-cordierite or indialite), which is obtained at higher temperatures (1350°C) and that of orthorhombic symmetry (β-cordierite or just cordierite), which is obtained at lower temperatures (1300°C). Apart from polymorphism, it is worth noting that commercial cordierites generally exhibit a pseudohexagonal lattice. Hence, analysis performed with synthetic cordierites allows comparison of their characteristics with those of natural minerals, showing intermediate behaviour between orthorhombic and hexagonal symmetries in most cases (Gonzalez, 2005).

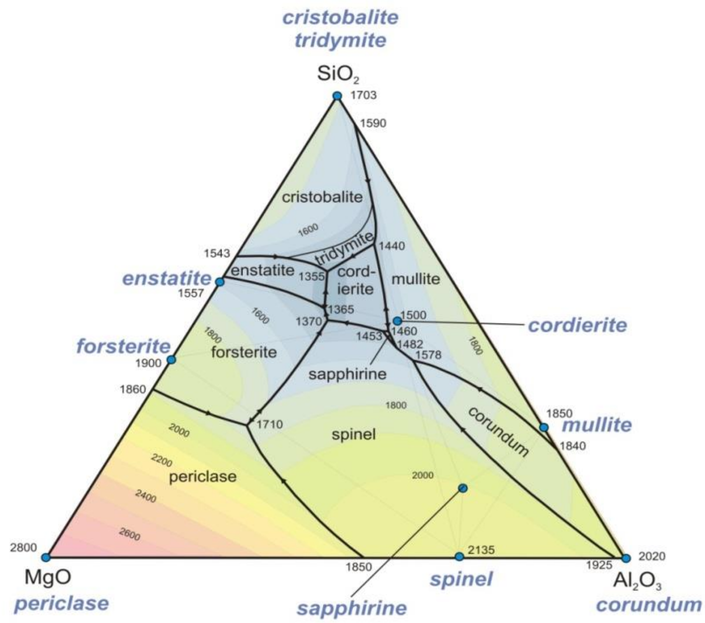

Figure 2.3 Ternary system of magnesium-aluminium-silicate (Camerucci et al., 2003)

Table 2.1 General properties of cordierite (Bertoldi et al., 2004).

Chemical Formula	$2MgO.3Al_2O_3.5SiO_2$
Empirical Formula	Mg2Al4Si5O18
Category	Mineral
Class	Silicates
Subclass	Cyclosilicates
Molecular Weight	584.95g
Essential Elements	Al, Mg, O, Si
Common Impurities	Mn, Fe, Ti, Ca, Na, K
Crystal System	Orthorhombic-dipyramidal (2/m, 2/m, 2/m)
Color	Birefringent (Different colour at different angle)
Melting Temperature	1460°C
Radioactivity	Not Reactive

2.2.1 Applications of Porous Cordierite

Cordierite is known to display very low thermal expansion as an attribute of an excellent thermal shock resistant material when it is subjected to rapid and severe changes in temperature. There is no doubt that cordierite is one of the potential ceramic filter (Ewais et al., 2009) material in meeting the demand of highly efficient particulate removal from a hot gas stream in a number of industrial process plants. The well-developed channels of the connected open pore structure give a filtration ability of these porous ceramics. Filters have been conventionally used in the shape of a long hollow cylinder "candle" with one closed end and with the flow inwards during filtration so that dust is collected on the external surface

Honeycomb catalytic support becomes one of the most significant applications of cordierite. This structure is increasingly used for many reactor applications, such as petrochemical industry, selective reduction of nitrogen oxides, selective hydrogenation of alcohols, automobile emission control and control of volatile organic compounds. The application of cordierite as monolith honeycomb carrier requires the synthesis by solid-state reaction from a mixture of various precursor oxides. This technique allows conformation of the monolithic structure with the sufficient refractoriness and thermal shock resistance to be used as catalytic support. (Gonzalez et al., 2005)

There are various techniques were proposed in the fabrication of porous cordierite, for examples, using the polymeric-sponge replication, (Senguttuvan et al., 2001), in-situ solidification of foamed, (Izuhara et al., 2000), sol-gel routes, (Guo et al., 2014), starch consolidation casting, (Alves et al., 1998), and gel-casting (Park et al., 2002). The selection of these techniques are based on the production cost and ease of processing route that will discussed in next section.

2.3 Methods to Fabricate Porous Cordierite

There are several processing routes to fabricate porous cordierite which depends on the various applications. The chosen method would encourage the properties of the porous cordierite. The developments of open-cell porous ceramics were highly versatile porous materials which are used mainly in applications that required fluid transport in the macrostructure. The general techniques used in the fabrications of ceramics foams has been review by Colombo (2006) which have three different methods; there are direct foaming of a liquid slurry, burn-out of fugitive pore formers or sacrificial template and replication of foam template.

2.3.1 Direct Foaming Methods

Porous materials are produce via direct foaming method by incorporating air into a suspension or liquid media, which is subsequently set in order to keep the structure of air bubbles created as shown in Figure 2.4. The consolidated foams are sintered at high temperature to obtained high strength of porous ceramic.

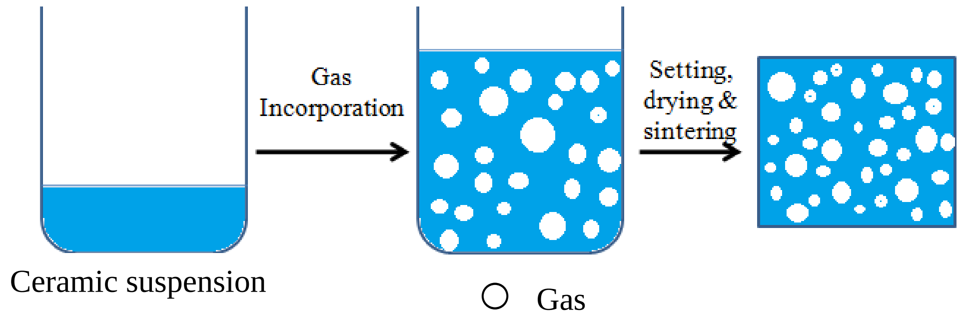

Figure 2.4 Scheme represent direct foaming route in porous ceramic (Studart et al.,2006)

The total porosity of directly foamed ceramics is proportional to the amount of gas incorporated into the suspension or liquid medium during the foaming process. While, the pore size would determine the stability of the wet foam before setting takes place. Thus, the most critical issue on direct foaming method is the approach used to stabilize the air bubbles incorporated within the initial suspension or liquid media.

Studart et al. (2006) has been review regarding to the fabrication of porous cordierite using direct foaming method. Park et al. (2002) are studied on the preparation of porous cordierite using gel-casting method and its feasibility as a filter. This foaming method are easy to control for the pore structure including pore size, porosity and pore type either open or closed (Saggio et al., 1992).

In-situ solidification is the other method that can be used in the fabrication of porous cordierite. This method of foamed slurries with different solid contents was studied by Izuhara et al. (2000) in order to achieve a highly porous cordierite green bodies. In their study, nitrogen gaseous (N_2) were introduced into the premixed slurries containing surfactant, monomer and gelation agents. The mechanical stirring employed produced bubbles and foam, which later creates porous body after sintered. Their finding showed that, the increasing of solid content increased the slurry viscosity, thus decreasing the total bubble volume in the foamed slurry. Samples were sintered in air at 1350 ºC showed that the pore diameter decreased as the solid content of the slurry increased.

Besides, monolithic-macroporous cordierite with 54% porosity was successfully fabricated by combining an epoxide-mediated sol-gel reaction with an ordinary hydrolysis-polycondensation of alkoxysilanes by Guo et al. (2014). Their study showed that propylene oxide (PO) accelerates the sol-gel transition of $MgO–Al_2O_3–SiO_2$ ternary system, while poly (acrylamide) (PAAm) mediates the phase separation of the system and improves the formation of the gel network. After heat-treatment, there are changes in the macroporous morphology of cordierite monoliths, where large and small interconnected pore structure with a dense skeleton was developed, whilst the shape of monoliths cordierite is maintained without cracks.

2.3.2 Sacrificial Template Method

The sacrificial template leads to porous materials displaying a negative replica of the original sacrificial template which is opposed to the positive morphology obtained from the replica technique. This technique usually consists of the preparation of biphasic composite comprising a continuous matrix of ceramic particles or ceramic precursors and a dispersed sacrificial phase that is initially homogeneously distribution throughout the matrix and ultimately extracted to generate pores within the microstructure as shown in Figure 2.5.

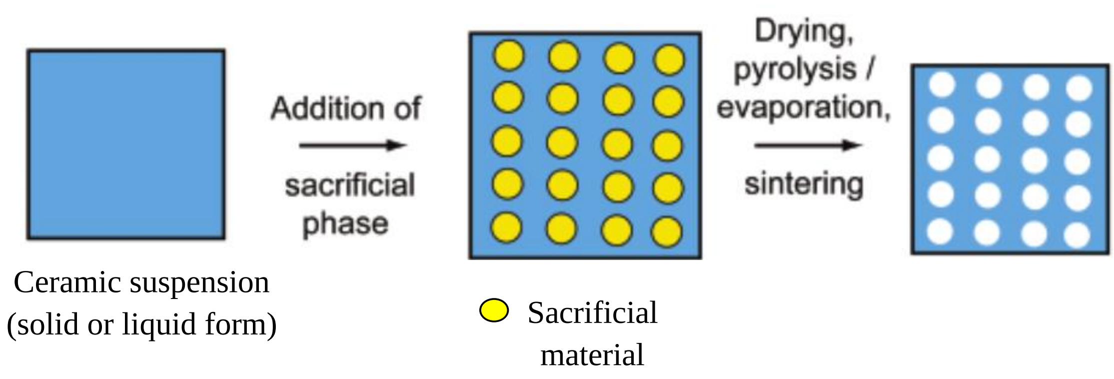

Figure 2.5 Scheme of sacrificial template of porous ceramics (Studart et al., 2006)

Park et al. (1998) are studied on the processing of porous cordierite bodies by starch consolidation. The structure and properties of porous ceramic are controlled by their processing. Some porosity can be introduced by manipulation of the particle size distribution or the interparticle forces or by deliberate incomplete densification during sintering (Morell 1997). Compare to the replica method, these methods do not assure reliable ceramic materials especially when a fine porous microstructure is required. Lyckfeidt and Ferreira (1998) showed that starch can be successfully used either as a pore former consolidator agent which enable porous very complex shaped alumina products to be directly formed form suspensions in nonporous mould. The dispersibilty and gelling capabilities of starch in water enable high solid loaded suspensions to be easily prepared and transformed into a rigid bodies that can be machined in the green state. The sintered bodies are enabling the design of porous textures and tailoring of the material to applications.

2.3.3 Replication Foam Template

The replica method is based on the impregnation of a cellular structure with a ceramic suspension or precursor solution in order to produce a porous ceramic exhibiting the same morphology as the original porous material as shown in Figure 2.6. This method can be categorized in two types of template naming as synthetic and natural cellular structure. Apart from all types of processing routes, replica technique is considered as the first method deliberately used for the production of porous ceramics. Schwartzwalder and Somers (1963) have been started using the polymeric sponges as templates to prepare ceramic cellular structures of various pore sizes, porosities and chemical compositions. Since then, the replica sponge technique has become the most popular method to produce macroporous ceramics and thus, extensively used in industry for varies applications. This is attributed to the simplicity and flexibility of the method.

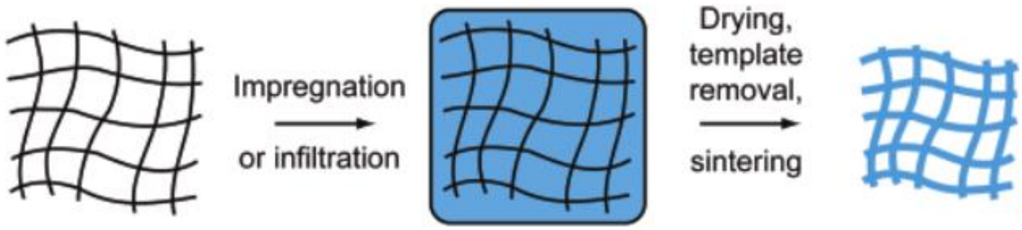

Figure 2.6 Scheme of replica technique of porous ceramic (Studart et al., 2006)

Senguttuvan et al. (2001) have employed the polymeric-sponge replication technique to produce alumina rich cordierite porous ceramics. The high alumina content used is to compensate the high thermal shock resistance requirement, thus a high alumina cordierite composition was evolved. In their study, the sintering temperature for cordierite foam was optimized around 1380 ºC with 68.4% porosity value.

Ewais et al., (2009) also fabricate the porous cordierite using a silica secondary resource (silica fumes) via replication sponge technique. The optimum conditions are revealed in order to get the cordierite phases. The sintering temperature of 1350°C and sintering time of 2 hour were the most appropriate conditions during the cordierite synthesis. Besides, Rodrigues Neto & Moreno (2007) studied on the rheological behavior of kaolin, talc and alumina suspension for manufacturing porous cordierite. The optimized conditions were 1350°C of sintering temperature at 1 hour sintering time.

2.3.3.1 Advantages of Replication Method

The replication method can be considered as the most popular technique in the fabrication of porous ceramics. The obvious reasons are by using this method porous ceramic can be very open structures with sufficient strength. This method can reached total open porosity levels within the range 40-95%. The sponge template method allows the possibility to fabricate porous materials with pore sizes in the ranges of 200 μm to 3mm. The high pore interconnectivity enhanced the permeability of fluids and gases through the porous structure.

Sponge replication method is an easy and flexible method with reproducibility and suitability of the foam to retain its shape during the fabrication method. The templates will completely burnout during the sintering process making these reticulated materials very suitable for high through-put filtration.

2.4 Process Involve in Replication Method of Porous Cordierite

Figure 2.7 shows the flowchart of the replication technique. This process involves coating a flexible, open-cell polymer foam with ceramic slurries. After removal of the excess slip by squeezing and subsequent drying, the polymer is burned out and the ceramic sintered in a single step (Saggio and Woyansky 1992).

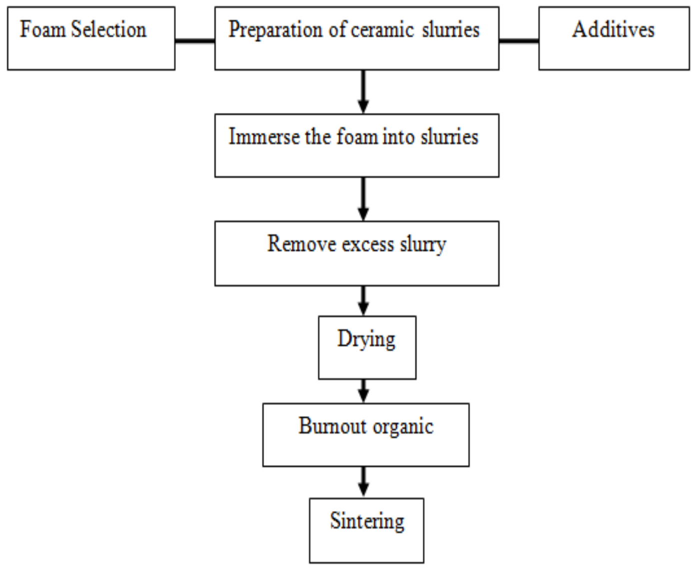

Figure 2.7 Flowchart of replication technique (Saggio and Woyansky 1992).

2.4.1 Selection of Foam Template

There are many different polymers can be used for the precursor foam which including polyurethane (PU), polyvinyl (chloride) (PVC), polystyrene (PS) and cellulose. Polyurethane (PU) is the most commonly used polymeric templates in the porous ceramic production. It is a cellular solid consisting of areas of PU polymer separated by voids (Parsons and Mountainm, 2007). The containing solid materials are referred to as struts and the voids may refer to as pores. The selection of the PU sponge is an important issue, as the physicochemical properties of these polymers may influence the sinterization of the ceramics. The sponge must burn out cleanly and completely during sintering without damaging the ceramic replica. The sponge commercially has pore size ranges from 2ppi to 60 ppi (pores per inches) and thus, this would determine the pore size of final product.

2.4.2 Preparation of Ceramic Slurry

The ceramic slurry is made of finely divided and homogeneously distributed ceramic particles, solvents and additives. The choices of any of these components are important in the formation of the slurry. The most important point for the slurry formation is the ability of the slurry to be fluid enough to impregnate the template (Dhara et al., 2006). The simplest classification divides fluids into the Newtonion and non-newtonion as shown in Figure 2.8. Newtonion fluid is a fluid whose viscosity is not influenced by the shear rate that is being applied to it. The viscosity remained constant as the shear changes. While, non-newtonion fluid is a fluid in which viscosity changes with the change in the shear rate that is being applied to it and the viscosity does not remain constant as the shear changes.

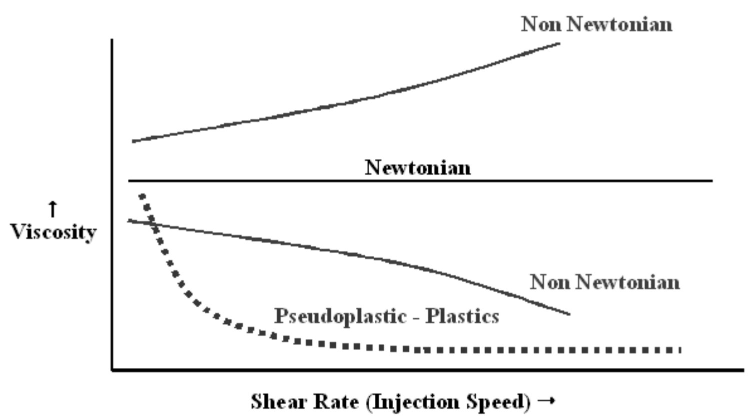

Figure 2.8 Fluid behaviors (Kulkarni, 2010)

As well knows, ceramic slurry must be viscous enough once impregnated to be retained on the template. According to Brown and Green (1994), to achieve quality of ceramic coating, the slurry must have the proper rheological characteristics, namely, pseudoplastic or shear-thinning behavior. The viscosity is low when a high shear rate is applied, however, the viscosity becomes high as the shear rate is low. This will allow the easy coating of substrate whilst after coating process, the increasing slurry viscosity allowing it to cling to the substrate. Thus, study on the slurry viscosity is one of the most important property that governs the microstructure and properties of porous ceramics.

2.4.4 Additives

In order to improve the formulation of slurry, additives were used to give better formation of porous ceramic. Additives that can be included in the formulation are dispersants, binders, rheological agents, antifoaming agents, wetting agents, flocculating agents, and air setting agents. The additives would stabilize the suspension, favor the uniform coating of the template, increase the adhesion of the slurry on the template and let the foam cell slurry coating of the template (Lewis, 1997)

2.4.4 Impregnation of Slurry into the Template

Once the polymeric template has been chosen and the ceramic slurry has been prepared, the next step is the impregnation of the template with the ceramic slurry. Typically, total impregnation of the polymeric template is achieved by compressing the foam, expulsing the air inside, and immersing it into the slurry. Then the foam is allowed to expend. Several compressions could be required, especially if the slurry is too viscous. No specific requirements are attached to this step (Studart et al., 2006).

Another key step of the preparation of porous ceramics is coming then: after being impregnated, it is required to expulse the excess of slurry from the polymeric sponge, to leave the cells open. Even if this can be done by manually pressing the foam, reproducibility and large scale production required the development of several processes dedicated to achieve this step. There are several methods that can be done. The impregnated foam can be compressed between to boards, centrifugated, or passed through rollers (Gallo et al., 2011).

2.4.5 Drying and Sintering

After the impregnated process were done, the foam is dried to evaporate the solvent and to leave a dense coating on the polymeric sponge, made of organics (additives) and ceramic particles physically bounded together. A specific attention has to be paid to regulate the humidity and temperature profiles to prevent from cracking. The typical temperature range is between 40 to 80°C with a humidity decreasing down to zero. However, it has to be noted that cracks could appear during the drying process. This also studied by Brown and Green (1994). Shrinkage of the slurry upon drying (while the PU template remains fixed) could cause cracks of the coating.

As mentioned previously, the sponge template that is usually used in this method is polyurethane (PU) foam. Sintering is applied both for removing the sponge template without collapsing the porous green body and to provide strength through the densification of particles (Munar et al., 2006). PU sponge will be removed from the specimen during sintering process to obtain the end product. Dressler (2009) had clearly explained the mechanism of how PU sponge was removed from the coated slurry during sintering. When the PU sponge and slurry was sintered, gradually the PU sponge was removed from the slurry remaining the empty space called hollow strut as shown in Figure 2.9. The mechanism of how hollow strut is obtained is shown in Figure 2.10. From the study, after heating to 260 ˚C, most of the PU sponge was removed from the