The Characterization of Silica-Nickel Oxide (SiO$_2$-NiO) Foam with Different NiO Composition and Sintering Temperatures

Syazwani Baharom
Sufizar Ahmad
Hariati Taib
Department of Materials and Design Engineering,
Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia,
86400 Parit Raja, Batu Pahat, Johor, Malaysia

ABSTRACT

The porous Silica-Nickel Oxide (SiO$_2$-NiO) ceramic had been fabricated by polymeric replication method, which produced high porosity with large interconnections. The influences of NiO composition on the morphology and properties of foams, including the compressive strength were studied. Polyurethane (PU) as the template was cut into a cylindrical shape of 12.5mm and 26.0 mm height. The PU template was impregnated in the prepared ceramic slurry which was a mixture of distilled water with Carboxymethyl Cellulose (CMC), Polyethylene Glycol (PEG), Silica (SiO$_2$) and Nickel Oxide (NiO). The composition of SiO$_2$ was fixed at 55 wt.% with varied NiO content of 2 wt.%, 4 wt.%, 6 wt.% and 8 wt.. The impregnated PU template was then dried in the drying oven and later the sintering process at temperatures of 1000ºC, 1100ºC and 1200ºC. The morphology of ceramic foam was analysed by Scanning Electron Microscopy (SEM) and Electron Dispersive X-ray Spectroscopy (EDS), while properties of sintered foam were determined by porosity and density test, and compressive test. The window cell size was observed within 200-800 µm with porosity and density results was in the range of 54.48-66.21% and 0.81-1.21 g/cm$^3$, respectively. The compressive strength of ceramic foam obtained was within 0.42-1.16 MPa.

Keywords: Reticulated, Engineering Ceramic, Gas Exchange, Polymeric Replication
Introduction

Highly porous ceramic materials are important for diverse applications such as membranes, molten metal filters, catalytic reaction supports, thermal insulation, cathodes, anodes and orthopaedic implants which lead to the development of numerous processing routes [1]. Various fabrication methods are available to prepare macro porous ceramic or ceramic foam such as direct foaming, sacrificial fugitives, polymer replication, freezing casting and partial sintering [2]. All these methods have their own merits and drawbacks. Thus, suitable methods selection plays as significant role in the success of porous product fabrication with relatively high strength, high resistance to chemical attack, high temperature resistance, and high structural uniformity [3]. As an example, polymer foam replication method can produce reticulated porous ceramic with ultra-high porosity and large interconnections [4].

The pore size can be easily controlled by varying the polymer size and it has been declared as its attractive value and thus become the reason for wider applications in industry [5]. In particular, Montanaro et al., 1998 stated that the porous network structures have relatively low mass, low density, low thermal conductivity, and even offer higher permeability [3]. Nowadays, the applications of porous ceramics are broadening in industrial market by adding additive as catalyst. The properties of ceramic foams which are sponge-like structures that consist of open accessible pore in the range of 10 to 100 per inch, with high interconnected window cells ranging from 75% up to 90% make them very attractive to be applied as catalyst supports [6]. There are few examples of supported metal catalysts which are nickel (Ni), platinum (Pt), palladium (Pd), rhodium (Rh), and ruthenium (Ru) [7]. All these elements are active and stable but very expensive. However, nickel based catalysts is the most favourable in the process of steam reforming of methane because of the high activity and plentiful resources of nickel [8].

In current study, SiO$_2$ and NiO were chosen as the starting materials in order to obtain porous ceramics products using the polymer replication template which requires a slurry preparation. The impregnation of polyurethane template (PU) was considered as crucial step because improper technique will affect the final product [9]. The research is focused on the effect of sintering temperature towards the morphology and mechanical properties of the porous SiO$_2$-NiO ceramic.

Experimental Procedure

The polymeric foam replication method was developed a decade ago and patented by Schwartzwalder and Somers [10]. The fabrication of porous ceramics by this method generally involves impregnation of an open-cell polymeric foam into a prepared ceramic slurry followed by burning-out of
polymeric foam through sintering process which yields ceramic foam as the replica of the original polymeric foam used [9]. The works flow were summarized in flowchart as shown in Figure 1.

**Results and Discussion**

The final product of porous ceramic depends on the starting material compositions and firing temperature. The morphology of the porous ceramic such as pore size, pore distribution, microstructure and compressive strength of the porous ceramic final product are hereby discussed.

**Characterisation of Foams**

Table 1 shows the composition of SiO$_2$ and NiO after the foam has been omitted during sintering process at 1200°C as analysed by Electron Dispersive X-ray Spectroscopy (EDS). It was observed that the mass of nickel has increased as the initial NiO composition was increased after sintering process. The increment of nickel content obtained by EDS confirmed that higher deposition of catalyst which is nickel particles on the surface of foam. Therefore, as deposition of catalyst on the bigger pores got higher, the higher goes the hydrogen generation rates [17].

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**Figure 1**: Fabrication steps of porous ceramic foam by polymer foam replication method

**Table 1**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica powder (SiO$_2$)</td>
<td>100 g</td>
</tr>
<tr>
<td>Nickel Oxide powder (NiO)</td>
<td>50 g</td>
</tr>
<tr>
<td>Carboxymethyl cellulose (CMC)</td>
<td>10 g</td>
</tr>
<tr>
<td>Polyethylene Glycol (PEG)</td>
<td>5 g</td>
</tr>
</tbody>
</table>

- Mixing in distilled water
- Impregnation of PU template into slurry
- Drying for 24 hours
- Sintering at 1000°C, 1100°C and 1200°C
Table 1: Results of EDS test for different NiO composition which has been sintered at 1200°C.

<table>
<thead>
<tr>
<th>Nickel Oxide Composition (wt.%)</th>
<th>Mass (%)</th>
<th>Silica (SiO₂)</th>
<th>Nickel (Ni)</th>
<th>Oxygen (O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>51.96</td>
<td>6.04</td>
<td>42.00</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>50.24</td>
<td>6.46</td>
<td>40.50</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>47.04</td>
<td>18.67</td>
<td>34.29</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>44.90</td>
<td>24.33</td>
<td>30.77</td>
<td></td>
</tr>
</tbody>
</table>

Thus, based on Table 1, it is confirmed that the content of both SiO₂ and NiO, as mixed did not show any reductions or decompositions upon sintering.

**Colour of Foams**

The final product of porous ceramic depends on the starting material compositions and firing temperature. The morphology of the porous ceramic such as pore size, pore distribution, microstructure and compressive strength of the porous ceramic final product are hereby discussed.

In this study, the colour of the samples changes when subjected to different sintering temperature. Figure 2 shows the colour difference of the SiO₂-NiO foam upon sintered at different temperatures. The colour change from dark grey to green was postulated due to the presence of NiO. However, it can be proved by the presence of excess NiO particles which shown in Figure 3. The changes of NiO colour from dark grey to green indicates that sintering started at below 773K which equal to 499.85°C, whereas with increasing green tones ranging from brown grey to grey-green and green-grey to olive green as sintering temperature increased [11]. The colour changes of the SiO₂-NiO foam with different sintering temperature was summarized in Table 2, while Figures 2(a), 2(b) and 2(c) represent the SiO₂-NiO foam after sintering.

Table 2: Colour changes of SiO₂-NiO foam at different sintering temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Colour of SiO₂-NiO foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>Dark grey</td>
</tr>
<tr>
<td>1100</td>
<td>Greenish grey</td>
</tr>
<tr>
<td>1200</td>
<td>Green</td>
</tr>
</tbody>
</table>
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Morphological Analyses
The morphology of the porous ceramic that has been sintered at 1000ºC, 1100ºC and 1200ºC observed under Scanning Electron Microscopy (SEM) was shown in Figure 3. The microstructure of the SiO2-NiO as can be seen in Figures 3(a), 3(b) and 3(c) consist of open pore, closed pore and interconnected. The open window cells are interconnected to each other by the struts. Black regions in the Figure 3 indicate the presence of open pore on the foam. The open pores on the porous structure of sample exhibit an interconnected by the struts.

Practically, SiO2-NiO foam which has been sintered at 1000ºC, 1100ºC and 1200ºC showed no obvious differences in their morphological structure and consisted of hollow particles of spherical shape and a large number of units having no regular form. The open pore or window cell size in this study were found to be within the range of 200 – 800 µm. The smallest window cell size was 262 µm and the window cell size increased up to 728 µm which was the highest window cell size observed. This result is found to be similar to the results obtained by the previous researchers [13,14] which obtained the macro porous structure of sintered ceramic foam in the range of more than 400 µm of pore size with high interconnectivity. Thus, SiO2-NiO foam fabricated by polymeric replication technique is suitable to be applied as catalyst support and other applications in other industries. However, the presence of closed cell numbers increased as the sintering temperature increased which can be seen in Figure 3(c). Therefore, it is suggested that, the excess slurry that hasn’t removed completely after impregnation of PU template process might contribute to the presence of closed cell. The excess slurry has bridging the struts of the sintered porous ceramic foams together[12].

Figure 2: Colour of SiO2-NiO foam after sintering at (a) 1000ºC, (b) 1100ºC, and (c) 1200ºC
Figure 3: Microstructure of sintered SiO$_2$-NiO foam at (a)1000°C, (b)1100°C and (c)1200°C with labelled of 1, 2, 3 for open pore, closed pore and interconnected, respectively.

Besides that, the morphology of porous structure which includes the content, dimensions, shapes and orientation of porosity can be adjusted by varying the initial slurry compositions [15]. As shown in Figure 3, the number of pore distribution decreased as the sintering temperature increases. However, the pore size would increased as the composition of NiO increase. Thus, the macroporous materials with a thick wall, low porosity and poor pore regularity are due to the excess content of oxide particles [16]. The powder such as particles on the surface of SiO$_2$-NiO foam as shown in Figure 4(a) is the excess of NiO particles where is the SiO$_2$-NiO foam sintered at 1200°C. In the other hand, Figure 4(b) shows a clearer image of SiO$_2$-NiO foam microstructure with irregular open pore shape, dense strut and excess NiO particles.
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Figure 4: The microstructure of SiO2-NiO foam with 8 wt.% of NiO at (a) 500X and (b) 1500X magnification

Porosity and Density Analyses
The porosity and density of sintered SiO2-NiO foam were obtained by applying the Archimedes’ principal as according to ASTM C773-88. The porosity and density of the SiO2-NiO foam effects due to varying NiO compositions were plotted as shown in Figures 5(a) and 5(b), respectively.

![Graph showing porosity and density changes with NiO composition and sintering temperature](image)

Figure 5: Effects of sintering temperature on porosity and bulk density of 55 wt.% of SiO2 with different NiO compositions
The result of porosity obtained in Figure 5(a) showed decreasing trend as the composition of NiO were increased due to decreasing number of open pore and presence of closed pore. The highest percentage of porosity was 66.21% for SiO$_2$-NiO foam with 2 wt.% of NiO, sintered at 1000°C. Meanwhile, the lowest value was 54.48% with addition of 8 wt.% NiO, sintered at 1200°C. As the sintering temperature increased, the number of porosity decreased due to the gradual occurrence formation of the neck in which the microstructure will be densified [18, 19]. The struts size measured in Figure 3(c) is 138.44 µm compared to the other two struts size which are 118.08 µm and 123.41 µm as observed in Figures 3(a) and 3(b). This is well supported by the morphology of sintered foam in Figure 3 which showed decreased number of open window as the sintering temperature increased. Furthermore, higher number of open pore cells were observed at lower temperature compared to the pore distribution at higher temperature as can be seen in Figure 3 which led to the higher porosity percentage at lower temperature. This might be due to the increasing of sintering temperature which affected the porosity when the holes left by the binder shrink and pore become smaller [27].

The trend of bulk density was found to be vice versa with the trend of porosity percentage. The density of SiO$_2$-NiO increased as the sintering temperature increased due to the decreased number in open pore. Therefore, as shown in Figure 5(b), the SiO$_2$-NiO foam which had been sintered at 1200°C showed the highest bulk density compare to the SiO$_2$-NiO foam sintered at 1000°C and 1100°C. The highest value of bulk density obtained was 1.21 g/cm$^3$ and the lowest value was 0.89 g/cm$^3$ which had been sintered at 1000°C. The decreasing trend of bulk density against temperature indicates the foaming process was more consistent and stable at higher temperature [20]. The decreasing of porosity percentage and open pore distribution correlated with the increasing of foam density as the sintering temperature increased.

**Compressive Strength Analyses**

The compressive strength of the SiO$_2$-NiO foam with 2 wt.%, 4 wt.%, 6 wt.%, and 8 wt.% NiO content sintered at 1000°C, 1100°C and 1200°C were plotted as in Figure 6.

From the graph in Figure 6, the lowest compressive strength obtained was 0.42 MPa for SiO$_2$-NiO foam with 2 wt.% of NiO content sintered at 1000°C, while the highest compressive strength was 1.16 MPa for SiO$_2$-NiO foam with 6 wt.% of NiO, sintered at 1200°C. The increasing strength of SiO$_2$-NiO increased as the composition of NiO increased due to the presence of closed pore at higher temperature as can be monitored by SEM in Figure 3. However, the trend of increased compressive strength for each composition was observed before decreasing at 8 wt.% of NiO composition for each
temperature. As the NiO composition increased, the viscosity of the slurry during slurry preparation increased and this might be one of the reason of decreasing trend observed for SiO$_2$-NiO foam with 8 wt.% of NiO. This is presumably that at lower composition, the slurry penetrated the PU template easily, while higher composition affects the impregnation process especially to retain their shapes and structures [13]. At higher composition, the slurry became saturated and unable to penetrate into the inner part of the foam away from the edges due to restriction of slurry flow as a result of high viscosity ceramic slurry.

Figure 6: The compressive strength of porous ceramic with different NiO content which was sintered at different temperatures

The compressive strength of SiO$_2$-NiO foams with 8 wt.% of NiO dropped significantly for every sintering temperature. The same trend was observed for fabricated SiO$_2$-NiO foams which have been sintered at 1000°C and 1100°C. Figures 7(a) and 7(b) show the stress-strain curve obtained for the SiO$_2$-NiO foam with 6 wt.% of NiO and 8 wt.% of NiO, respectively.

Figure 7 shows that both of the SiO$_2$-NiO foams exhibit brittle behaviour which is remarked by the linear increment of stress before the value dropped. The linear increase corresponds to the typical linear elastic behaviour for brittle foam before progressive cells collapse at solid phase by brittle crushing of the struts between the pores. Moreover, brittle fracture is also correlated with crystalline structure which has lower modulus of elasticity compared to plastic and polymer [21].

Pore distributions also affect the mechanical properties of the porous ceramic [22]. As expected, the compressive strength of the SiO$_2$-NiO foam was increased as the temperature increased. A discussion by [23] stated that, the mechanical properties of porous ceramics were controlled by the number of porosity and will decrease with increasing pore volume fraction.
Additionally, the dropped of compressive strength might be due to higher NiO loading. This is well supported by Hermida et al., 2013, Cai et al., 2014 and Nikolić et al., 2015 which noted that structural collapse and significant drop in the well-defined framework mesoporosity are due to local blockage of pore channels and agglomeration of higher nickel nanoparticles loading at high temperature [24, 28, 29]. Besides that, the mechanical strength of the sintered body is highly dependent on the foam's microstructure, especially on defects such as pores and cracks [25]. The presence of cracks on the surface of SiO$_2$-NiO foam as shown in Figure 8 would lower the mechanical properties of the sintered foam.

Figure 7: Stress-strain curve for different NiO composition at 1200°C

Figure 8: Cracks as observed on the surface of SiO$_2$-NiO foam with 8 wt.% of NiO composition sintered at 1200°C
The presence of triangularly shaped hole inside the struts contribute to stress concentration at the edges, as well as cracks which is the other reason for limited strength of SiO$_2$-NiO foam [26]. Porous foam with low strength and fracture toughness is resulted due to foam fabrication technique of replication technique. High number of porosity and thin skeletons limit their structural application and thus more sensitive towards structural stress [27].

**Conclusion**

Polymeric foam replication method is one of the fabrication methods which are capable of producing the final porous ceramic with larger pore size with open window cell in range of 200-800 µm. The pore distribution decreased as the sintering temperature is increased from 1000ºC to 1200ºC. The decreasing of open pore cells observed on the morphology of sintered foam affected the result of porosity percentage and density. Decreasing trend of porosity percentage was observed as the sintering temperature and NiO composition increased while the trend for bulk density indicates otherwise. Moreover, the compressive strength dropped at 8 wt.% of NiO content due to the excess nickel content. Thus, it can be concluded that the best sintering temperature is 1200ºC with 6 wt.% of NiO content. Fabrication of SiO$_2$-NiO foam using polymeric replication technique is capable of producing high porous microstructure and of resulting good properties with lower fabrication cost which can compete with other techniques such as direct foaming, gel-casting and sacrificial fugitives. A further study of SiO$_2$-NiO foam in methane reforming will be carried out.

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**References**


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