The effect of thermal and organic additive in morphology of ceramic based silicate

J Ginting, N Bangun, H Br Sembiring and N K Putri

Faculty of Sciences and Mathematic, University of Sumatera Utara, Medan, Indonesia

Email: nabilakarina97@gmail.com

Abstract. M-Silicate (M = Mg, Ca) has been prepared by exchange metal reaction from M-Chloride salts and sodium silicate. The resulting white solid of chloride salts then heated at 700, 800, 900 and 1000 °C. Due to increase the porosity of M-Silicate, 1,2-propanediol, oleic acid and glycerol were added, then formed M-silicates were heated at 800 °C. Then, obtained white solid M-Silicates were characterized by Scanning Electron Microscopy (SEM). SEM images show the variance of surface morphology when the temperature increases. The addition of organic compounds is involved in surface modification.

1. Introduction

Preparation of Silicate salts had been done in many sources and ways. The modification of its surface and properties could be achieved effectively with low-cost and the reusable silicate is mostly used as adsorbent [1-3]. Silicates are inorganic components which can be easily prepared into monolith or porous material [4]. The porosity of silicates can be enlarged for applications in industries. High temperature will increase its porosity and it classified as ceramics [5]. High temperature can change the surface texture, roughness and shapes of materials [6].

The combination of silicate with organic compound serves an opportunity to increase the stabilities of materials [7]. This combination of silicate and organic additive produce silicates with high medical stability [8]. Preparation of silicate material will improve its functional surface and ability to interact with different molecules that was obtained by combination of silicates and organic compound [9]. The combination of silica with organic compound addition, such as chitosan and methacylic acid, in sol-gel methods exhibit the formation of porous structures and improve its functional contact surface area [10].

In this paper, we report our finding about the effect of heat and organic additives which are glycerol, 1,2-propanediol and oleic acid in preparation of M-silicate (M= Mg, Ca). Oleic acid was used to represent monounsaturated acid and long chain substance. While glycerol and 1,2-propanediol were used to compare the surface morphology, considering they were oleic acid derivative. The surface morphology was then observed by scanning electron microscopy (SEM).

2. Experiments

2.1. Materials and Instruments
2.1.1. **Materials.** MgCl$_2$, CaCl$_2$, sodium silicate, 1,2-propanediol, glycerol and oleic acid

2.1.2. **Instruments.** Surface morphology and elemental analysis were analyzed by SEM-EDX, (EVO MA-10 Bruker 129 ev Zeiss).

2.2. **Preparation of Ceramic Based Silicate**

2.2.1. **Effect of Heating.** Four kinds of MgSiO$_3$ were prepared by mixing an appropriate amount of MgCl$_2$ in aqueous solution with sodium silicate by stirring in room temperature for 3 h. Then, the precipitated white MgSiO$_3$ was heated in a furnace at 700 °C (1), 800 °C (2), 900 °C (3) and 1000 °C (4). The surface morphology and elemental analysis of (1), (2), (3) and (4) were characterized and analysed by Scanning Electron Microscopy (SEM) integrated with Energy Dispersive X-ray (EDX) as elemental analysis. The procedure was repeated to prepare four kinds of CaSiO$_3$ (5), (6), (7) and (8) by replacing MgCl$_2$ with CaCl$_2$.

2.2.2. **Effect of organic additive.** The other three MgSiO$_3$ were prepared with different methods with additions of three kinds of organic substances. An appropriate amount of MgCl$_2$ in aqueous solution was added to sodium silicate while stirred in room temperature. After 3 h, 10% 1,2-propanediol (9), glycerol (10) and oleic acid (11) was added then stirred for another 30 min. The precipitated white solid separated then heated in a furnace at 800 °C. The surface morphology and elemental analysis were measured by SEM-EDX. The procedure was repeated to prepare three other kinds of CaSiO$_3$ (12), (13) and (14) by replacing MgCl$_2$ with CaCl$_2$.

The summary of preparation ceramic based silicates is explained on table 1.

| Code | M-Silicates, M = Mg, Ca (M-Cl$_2$ + Na$_2$SiO$_3$) | Heated at | Organic additive (10%) |
|------|-----------------------------------------------|-----------|------------------------|
| (1)  | MgSiO$_3$                                     | 700 °C    | -                      |
| (2)  | MgSiO$_3$                                     | 800 °C    | -                      |
| (3)  | MgSiO$_3$                                     | 900 °C    | -                      |
| (4)  | MgSiO$_3$                                     | 1000 °C   | -                      |
| (5)  | CaSiO$_3$                                     | 700 °C    | -                      |
| (6)  | CaSiO$_3$                                     | 800 °C    | -                      |
| (7)  | CaSiO$_3$                                     | 900 °C    | -                      |
| (8)  | CaSiO$_3$                                     | 1000 °C   | -                      |
| (9)  | MgSiO$_3$                                     | 800 °C    | 1,2-propanediol        |
| (10) | MgSiO$_3$                                     | 800 °C    | Glycerol               |
| (11) | MgSiO$_3$                                     | 800 °C    | Oleic acid             |
| (12) | CaSiO$_3$                                     | 800 °C    | 1,2-propanediol        |
| (13) | CaSiO$_3$                                     | 800 °C    | Glycerol               |
| (14) | CaSiO$_3$                                     | 800 °C    | Oleic acid             |

3. **Results and Discussions**

3.1. **EDX spectra**

The reaction between sodium silicate and M-Cl$_2$ (M = Mg, Ca) are shown below.

- \[
\text{Na}_2\text{SiO}_3(aq) + \text{MgCl}_2(s) \rightarrow \text{MgSiO}_3(s) + 2 \text{NaCl}(aq)
\]

- \[
\text{Na}_2\text{SiO}_3(aq) + \text{CaCl}_2(s) \rightarrow \text{CaSiO}_3(s) + 2 \text{NaCl}(aq)
\]
Energy Dispersive X-ray spectra represent the element that contains in M-silicates as the confirmation of exchange metal reaction had occur. The EDX spectra of M-silicates are shown in figure 1. The EDX spectra of Mg-silicate (a) that show the presence of O, Mg and Si elements confirm that Mg-silicate already performed while the EDX spectra of Ca-silicate (b) show the presence of Ca, O and Si.

![EDX spectra of (a) Mg-silicate and (b) Ca-silicate](image)

**Figure 1.** EDX spectra of (a) Mg-silicate and (b) Ca-silicate

3.2. **SEM image**

3.2.1. **Effect of heating.** The SEM images of Mg-Silicate and Ca-silicate are shown in figures 2 and 3, respectively. The heat affected the change of surface morphology for both Mg-silicate and Ca-silicate.

![SEM images of Mg-Silicate with temperature variation](image)

**Figure 2.** The SEM images of Mg-Silicate with temperature variation (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C
From figure 2(a) displays the surface area with close pore. The surface is rough and has a hard texture. Figure 2(b) shows a rough surface with agglomeration and looks bumpy. Figure 2(c) shows an agglomerated surface. The fibre looks filling the surface of figure 2(c). While, figure 2(d) also show an agglomerated and rough surface.

The variation of temperature during preparation of Mg-silicate affected in surface morphology. Most of the Mg-silicates surface represent roughness and agglomeration, but the term of the effect is depending on each treatment temperature.

Ca-silicates morphology shows fibre and yarn surface. The surface of Ca-silicate displays a soft texture that is represented by figure 3. Figures 3(a) and 3(b) display a soft net surface with small porous. Figure 3(c) displays a wavy net surface with the form of rectangular porous in almost part while figure 3(d) represents the agglomeration and a very wavy surface. From both Mg-silicate and Ca-silicate images, the size of pore increases with the increasing temperature.

![Figure 3](image)

**Figure 3.** The SEM image of Ca-silicate with temperature variation (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C

3.2.2. Effect of organic additives. To increase the porosity of M-silicate, organic substance addition such as 1,2-propanediol, glycerol and oleic acid were added to the mixture then M-silicate heated at 800 °C. M-silicate was characterized using SEM. The SEM images of Mg-silicate are shown in figure 4 while the SEM images of Ca-silicate are shown in figure 5.
Figures 4(a) and 5(a) have the same of large surface morphology and there is a hole like in the surface. Figures 4(b) and 5(b) show a shape of pores figures 4(c) and 5(c) have a detached part in the surface. The organic substance that had been added to the material leads to a difference characteristic in forming the surface area. 1,2-propanediol will produce wider surface, while glycerol will enhance the pore while oleic acid will split the surface.

4. Conclusions
Heat will affect the surface morphology of M-silicate (M= Mg, Ca). The porous size increase with the increasing of temperature. While organic substances addition changes the surface morphology of M-silicate (M= Mg, Ca), the results still depends of the properties of organic substance that used.

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