Effect of Thermal Treatment on Natural Dolomite

Siti Fatimah Azzahran Abdullah1,2, Siti Shuhadah Md Saleh1,2, Nur Farahiyah Mohammad1,4, Mohd Sobri Idris3 and H. R. Salisu2

1Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, Jejawi 3, 02600 Arau, Perlis, Malaysia
2Biomedical and Nanotechnology Research Group, Center of Excellence Geopolymer and Green Technology (CEGeoTech), Universiti Malaysia Perlis, 01000 Kangar, Perlis, Malaysia
3Medical Device and Life Science Cluster, Sport Engineering Research Centre, Universiti Malaysia Perlis, Pauh Putra Campus, 02600 Arau, Perlis, Malaysia
4Faculty of Electronic Engineering Technology, Pauh Putra Campus, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia
5Department of Polymer and Textile Engineering, Faculty of Engineering, Ahmadu Bello University, Zaria, Nigeria

Abstract. Dolomite is a mineral material that is formed from limestone which is mostly contains the calcite (CaCO3) and magnesite (MgCO3). This paper aimed to study on thermal decomposition of dolomite under air atmosphere. Calcination of dolomite was carried out by using furnace with heating rate of 10 °C/minute in an air atmosphere. The different temperature of calcination was varied at 400 °C, 600 °C, 800 °C, and 1000 °C within 6 hours. Phase analysis (XRD) and functional group analysis (FTIR) were carried out to analysis the dolomite after calcination. Microstructural (SEM) and Energy Dispersive X-ray (EDX) analysis showed that the main constituents of pure dolomite include CaCO3 (calcite), MgCO3 (magnesite), CaO, and MgO. From the results, XRD showed that the high intensity of CaO and MgO at 800 - 1000 °C was much stronger than that of dolomite at 400 - 600 °C. In addition, FTIR presents strong and intense bands are observed at 3632.23 and 3694.03 cm⁻¹ (800 °C), and also 3694.03 and 3633.60 cm⁻¹ (1000 °C) due to the calcium oxide.

1 Introduction

Dolomite, CaMg( CO3)2 is an abundant carbonate material and it coexists with calcite in nature. It has a hexagonal crystalline network. The quantity of calcium and magnesium present in most dolomite is equal but sometimes one element have greater presence than the other. Calcination of dolomite at higher temperature (> 450 °C) leads to covers covering of pores and the surface topography of the sample has no significant changes.

Dolomite composed of CaCO3 and MgCO3 which have different decomposition behaviour. Calcination of MgCO3 occur at lower temperature and much faster than CaCO3. During this process, the porosity of the dolomite structure largely increases [1,2]. Extra pore volume is more formed due to lower molar volume of MgO compared to MgCO3. As the temperature increases, calcination of CaCO3 takes place once MgCO3 fully calcined and the particle achieves its maximum porosity and specific surface area.

Calcination is to transform the carbonate minerals to oxide form. Calcination of dolomite is divided into two stages, (1) and (2), which are lower temperature calcination and higher temperature calcination. At low temperature, Calcite (CaCO3) and Magnesium Oxide (MgO) will form. While at higher temperature, calcite decompose to Calcium Oxide (CaO).

\[
\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaCO}_3 + \text{MgO} + 2\text{CO}_2 \quad (1)
\]

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (2)
\]

Dolomite powders contain lines that related to dolomite substance MgCa(CO3)2, while calcined dolomite powders contains greater crystal phase of MgO with extremely improved crystallization. Calcination of dolomite at a temperature between 800 °C and 1000 °C is for decarbonation of dolomites to remove CO2 ions which will generate reaction CaO and MgO [2,3]. The lime and periclase are the main crystalline phase in calcined dolomite from the decarbonation process.

\[
\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2 \quad (3)
\]

Minerals such as calcite and dolomite are often related to impurities which would affect the calcination process [4]. Those impurities are usually manganese or iron for calcite and dolomite. Impurities can be found with the iron carbonate

3 Corresponding author : shuhadah@unimap.edu.my
by direct substitution of iron in the lattice of the mineral or as a different mineral such as calcite and dolomite. Furthermore, upon deposition the crystal lattice of dolomite is converted from rhombohedral lattice to cubic lattice [5].

2 Experimental

2.1 Material

Dolomite was used as the raw material in this study. The dolomite was purchased from Perlis Dolomite Industries Sdn. Bhd., Perlis, Malaysia. The chemical composition of dolomite was tabulated in Table 1. The size of the dolomite was sieved at 63 µm. Before the sieving process, the solid dolomite was blended to obtain the small particles, regular shape and size.

| Chemical Compound | Composition (wt %) |
|-------------------|-------------------|
| CaO               | 80.21             |
| Al₂O₃             | 1.52              |
| SiO₂              | 2.50              |
| Fe₂O₃             | 0.15              |
| MgO               | 15.50             |
| CuO               | 0.07              |
| MnO               | 0.02              |

2.2 Mixing Parameter

In this study, dolomite was used as the raw material. It was collected from Perlis Dolomite Industries Sdn. Bhd., Perlis, Malaysia. Firstly, dolomite was sieved using 63 µm in order to obtain the regular shape form. In order to determine the effect of thermal treatment, the dolomite powder was subjected with different temperature varied at 400 °C, 600 °C, 800 °C and 1000 °C for 6 hours. After calcination process, the powder was characterized with X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR).

2.3 Test and Analysis Methods

The chemical composition of dolomite was determined by using X-ray Fluorescence (XRF) spectrometer with brand name of PAN analytic PW4030 model type MiniPAL-4 with MiniPal software. The sample was loaded in the chamber of the spectrometer and operated at maximum voltage of 30kV and a maximum current of 1 mA was applied to produce X-ray to excite the sample for a pre-set time (10 minutes). Scanning Electron Microscope (SEM) used to investigate the morphology of the treated dolomite. After placing the dolomite sample on the aluminum stub, it went through coating process. Sputter-coater Q150R S was used to coat the material by a conductive material which is platinum for 8 minutes to avoid charge buildup. After coating, the stub was placed in Scanning Electron Microscopy. The microstructural properties of dolomite were tested by Scanning Electron Microscope JEOL JSM-6460LA. XRD was used to characterize the powder compound in order to confirm the existence of element after treatment process. The Expert High Score Plus software was used to analysis the XRD data. Specimens were prepared in powder form. The powder was examined via X-ray diffraction machine (Bruker D8 Advanced) using CuKα radian (λ = 1.5406 nm) as an X-rays source. The XRD scans for each sample are taken places from 10° and 90° of 2θ scale. Functional group of dolomites was identified using Perkin Elmer FTIR Spectrum RXI Spectrometer. 3 mg of powdered specimen were put into a mold. The powdered specimen was scanned from 500 cm⁻¹ to 4000 cm⁻¹ with resolution of 4 cm⁻¹. Sample spectrum was collected after collecting the background spectrum.
3 Results and Discussion

3.1 Microstructural Analysis of Dolomite

Surface morphology of pure dolomite were characterized by using SEM. Fig 1 shows SEM micrograph of pure dolomite. These micrographs clearly illustrate the different particle size of pure dolomite powder. Pure dolomite that received from Perlis Dolomite Industries contains wide range of particle size and thus sieving was carried out to obtain uniform particle size. As displayed in Fig the initial dolomite powders are in block-like shape [5] with clear edges.

![SEM micrograph of pure dolomite](image)

**Fig. 1.** SEM micrograph of pure dolomite.

Elemental composition of pure dolomite was characterized by using Energy Dispersive X-ray (EDX). Figure 2 shows the result of EDX of dolomite. Usually, minerals such as calcite and dolomite are often related to impurities which would affect the calcination process [3]. Those impurities are usually manganese or iron for calcite and dolomite. But the results obtained from EDX illustrated the presence of calcium (Ca) and magnesium (Mg) in dolomite. Thus, these dolomite particles have 100% of purity.

![Energy Dispersive X-ray of Pure Dolomite](image)

**Fig. 2.** Energy Dispersive X-ray of Pure Dolomite.

3.2 XRD Analysis of the Pure Dolomite and Calcined Dolomite

Fig 3 shows the X-ray diffraction analysis of dolomite. Dolomite contains mineral dolomite (CaCO₃·MgCO₃), calcite (CaCO₃) and also some impurities such as hematite (Fe₂O₃) and feldspar (silica minerals) [6]. For the natural dolomite, the diffraction peaks clearly observed at 31.5, 41.07, 44.8, 50.5 and 51.0 which correspond approximately to the 30.93, 41.12, 44.95 and 50.52 respectively for the standard [3,7].
Fig. 3. XRD analysis of dolomite.

Fig. 4 shows the dolomite were calcined at 6 hour with different temperature varied from 400 °C to 1000 °C. After calcination at 400 °C and 600 °C, there were no obvious change on its XRD patterns compared with that of natural dolomite. Obviously, there would be no significant decomposition of dolomite at these temperature. However, for the XRD patterns of dolomite calcined at higher temperatures, the peaks shifted were detected at 29.9, 43.5, 47.5 and 50.5 were corresponding to the calcium oxide. Meanwhile, the peaks at 34.0, 43.5 and 48.5 were observed that contributed to the magnesium oxide. Moreover, the crystallinity of CaO and MgO at 800 and 1000 °C was much stronger than that of dolomite at 400 and 600 °C. It indicates that at high temperature, the crystallization was further occurred. Besides, Mandrino et al. [9] found that the thermal treatment under 700 °C had a small influence to the dolomite characteristics compared to the natural dolomite.

Fig. 4. XRD analysis of dolomite with different temperature (400 °C, 600 °C, 800 °C and 1000 °C).
3.3 FTIR Analysis of the Pure Dolomite and Calcined Dolomite

Fig. 5 presents the FTIR spectra of natural dolomite. The spectrum of natural dolomite showed two peaks at 717.68 and 873.26 cm$^{-1}$. The peak at 717.68 cm$^{-1}$ was represented to the bending mode of CO$_3^{2-}$ part of dolomite [10]. Later, the peak at 873.26 cm$^{-1}$ was significant to the carbonate bending mode. However, when the temperature up to 800 °C, the dolomite decomposed to oxides of calcium and magnesium. Moreover, the FTIR spectra of CaO and MgO were shown as increasing the temperature. In addition, a little amount of adsorbed surface water was also observed in the FTIR spectra by the presence of the broad OH stretching of hydrated carbonate at 3218.34 cm$^{-1}$.

![FTIR Analysis of Natural Dolomite](image)

Fig. 5. FTIR analysis of natural dolomite.

Figure 6 shows the FTIR spectra for dolomites with different temperature varied form 400 °C, 600 °C, 800 °C and 1000 °C. The peak at 1421.09 cm$^{-1}$ were clearly appeared show the structural transformation of natural dolomite to calcium and magnesium oxides. However, after calcination, the band at 1416.15 cm$^{-1}$ at 400 °C was shifts to 1404.66 cm$^{-1}$ due to the presence of calcium and magnesium oxides [11]. Moreover, strong and intense bands are observed at 3632.23 and 3690.98 cm$^{-1}$ (800 °C), and also 3694.03 and 3633.60 cm$^{-1}$ (1000 °C) due to the calcium oxide. In addition, the weak bands at 868.70 – 865.76 were observed in all calcination dolomite. The weak bands at 865.76 and 1074.50 cm$^{-1}$ in 1000 °C combine together to form a strong and broad band after calcination process thus introducing to the effect of impurities such as silicates on the dolomite structure.
Fig. 6. FTIR analysis of dolomite with different temperature (400 °C, 600 °C, 800 °C and 1000 °C).

4 Conclusion

As the conclusion, calcination of dolomite occurs in two stage reaction which started to decomposed at 600 °C and complete calcination at 800 °C. The FTIR analysis confirmed that the structural transformation of natural dolomite to the calcium and magnesium oxide form, and the results of XRD analysis showed that calcium and magnesium oxide were clearly observed at 800 °C and 1000 °C compared to the 400 and 600 °C. This shows that calcination of dolomite has better with increasing calcination temperature.

The authors of the present work wish to acknowledge the funding by Fundamental Research Grant Scheme (FRGS/1/2019/UNIMAP) sponsored by Ministry of Education Malaysia. Special thanks to those who contributed to this project directly or indirectly.

References

1. Herce, C., S. Stendardo, and Cortes, C., Chemical Engineering Journal, 262, 18-28 (2015)
2. Yang, T., Z. Zhang, H. Zhu, W. Zhang, Y. Gao, X. Zhang, and Wu, Q. Construction and Building Materials, 211, 329-336 (2019)
3. Garcia, A. C., M. Latifi, and C., J. Minerals Engineering, 150 (2020)
4. Maitra, S., A. Choudhury, H. S. Das, and Pramanik, M. J., Journal of Materials Science, 40, 4749-4751 (2005)
5. Beruto, D. T., R. Vacchiattini, and Giordani, M. Thermochimica Acta, 404, 25-33 (2003)
6. Wulandari, S. W., P. M. Adinata, and F., A. AIP Conference Proceedings (2018)
7. Adesakin A.O., Ajayi O.O., Imosili P.E., Atahdaniel B.E. and Olusunle S.O.O, Chemistry and Materials Research, 3, 2224-3224 (2013)
8. A., S. A., Ramesh, S., Bushroua, A. R., Ching, Y. C., Sopyan, I., Maleque, M. A., Sutharsini, U. Ceramics International, 44(2), 1802-1811 (2018)
9. Mandrino, D., Paulin, I., Kržmanc, M. M., & Škapin, S. D., Journal of Thermal Analysis and Calorimetry, 131 (2), 1125-1134 (2017)
10. Tamaddon, F., Tayefi, M., Hosseini, E., & Zare, E. Journal of Molecular Catalysis A: Chemical, 366, 36-42 (2013)
11. Mohammed, M. A. A., Salmiaton, A., Wan Azlina, W. A. K. G., Mohamad Amran, M. S., & Taufiq-Yap, Y. H. Journal of Energy, 2013, 1-8 (2013)