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Research paper

Characterization of Fe_2O_3/Mn_2O_3 Oxygen Carrier for Chemical Looping Combustion Prepared by Dry Impregnation Method

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Abstract

Recently, bauxite waste was found as newly sourced of Fe-based oxygen carrier in chemical looping combustion (CLC) since it contains high Fe and capable to be used as oxygen carrier at low cost. This study focuses on synthesizing and characterizing the bauxite waste that found in Malaysia with Mn_2O_3 using dry impregnation method and study the feasibility of this bauxite waste as oxygen carrier. Results show the combination of bauxite waste – Mn_2O_3 at 900°C produces crystallite size 21 nm with the presence of Fe-Mn, stable Al_2O_3 and Ti elements that can improve the reactivity of Fe-Mn oxygen carrier. Moreover, Al_2O_3 that contains naturally in bauxite waste can acts as supported material for Fe-Mn oxygen carrier in order to increase performance in CLC process. Therefore, this powder was successfully synthesized using dry impregnation method at calcination temperature 900°C and fit to be tested in a fluidized bed reactor to simulate the CLC process since it has smaller and stable particle size.

Keywords: *bauxite waste, dry impregnation method, Fe-based oxygen carrier, Fe-Mn.*

1. Introduction

Chemical looping combustion (CLC) is one of the carbon capturing technology, that used oxygen carrier to provide an oxygen during combustion process inside fuel reactor. During the combustion process, oxygen carrier undergoes reduction reaction process and H_2O is condensed and subsequently produce pure CO_2 prior released from fuel reactor. Then, this oxygen carrier flows to air reactor for oxidizing process prior flow back to the fuel reactor. This reduction and oxidation (redox) reaction repeatedly occurs until the properties of oxygen carrier degrade [1-5]. In CLC, CO_2 can be captured and reduce energy penalty to 4.1% [6]. Therefore, CLC is a promising carbon capturing technology that can capture CO_2 at low cost without requiring high-energy consumption and special equipment.
In CLC, oxygen carrier plays an important role since it can affect performance and efficiency of CLC. The good characteristics of oxygen carrier are full conversion of fuel to H_2O and CO_2, high reactivity and regenerability during redox reaction so that the replacement of oxygen carriers inside fuel reactors can be reduced, can resist to agglomeration with high circulation of particles during the process, minimum carbon formation, simple, low manufacturing cost and minimum environmental impact [7]. There are 5 metals based commonly used as oxygen carriers such as Fe, Ni, Cu, Mn and Co based [8]. From previous studies, Cu-based and Ni-based shows good performance as oxygen carriers. However, Cu-based cannot withstand at high temperature because it has low melting point temperature and Ni is expensive and safety measures is needed to handle waste of this material due to its hazardousness [1-3,9]. Mn-based has low reactivity with fuels that can reduce efficiency of CLC system. Meanwhile the Co-based is highly cost and toxic to the nature [3,10]. Nevertheless, Fe-based is non-hazardous, cheap, and less prone to the carbon formation. Therefore, it can reduce the total operational cost especially for CLC using coal as fuel. However, particle agglomeration becomes an issue after several cycles when using pure metal oxide as oxygen carrier [3]. Thus, durability and performance of this oxygen carrier can be increase by using supported materials such as Al_2O_3, $MgAl_2O_4$, SiO_2, TiO_2 and YSZ [11-13]. Nevertheless, low cost materials were used continuously in CLC that used coal as fuel [5]. So, replacing the used oxygen carrier would not be an issue especially from economical aspect. Iron ore and ilmenite were used continuously as natural resources of oxygen carrier in CLC process. Even though iron ore and ilmenite shows a good fluidization properties and minimum attrition but most of that materials need to undergo several processes prior to be used as oxygen carrier.
Therefore, researchers were discovering the industrial waste as potential newly sources of Fe-based oxygen carrier in CLC process. Therefore, one of the industrial waste that have high Fe-content is a bauxite waste. Mendiara et al. [5] stated that bauxite waste shows good performance as oxygen carrier due to its composition that contains Fe_2O_3 and TiO_2. In addition, Kong et al. [14] discovered that bauxite waste release more oxygen during redox reactions, hence increases the reactivity in CLC. Based on Chen et al. [15], combining metal oxide with manganese oxide is capable to increase fuel conversion at high temperature. Azimi et al. [16] studied the combination of Fe-Mn oxide and the result shows, these two combination materials are promising oxide combination since the oxidized form of hematite and bixbyite can be reduce to magnetite and hasumannite. Moreover, Haider et al [17] studied the hematite with Mn_2O_3 at temperature of 950°C and result shows the combination of Fe-Mn at this temperature has an effect by increasing the cycle numbers of the process. Furthermore, Mn_2O_3 also starts to yield at temperature more than 800°C [18].

There were many methods that used to produce oxygen carrier such as ball milling, freeze granulation, gel combustion, and sol gel method [19-21]. However, dry impregnation method was found to be a method that can improve the chemical reactivity and mechanical properties of oxygen carrier.

Thus, this research focused on synthesizing and characterizing bauxite waste that contains Fe_2O_3 with Mn_2O_3 using dry impregnation method and investigates the feasibility study of obtained bauxite waste as Fe_2O_3 with Mn_2O_3 as an oxygen carrier. In this study, calcination temperature was varied in order to determine the optimum formation of bauxite waste as Fe_2O_3 with Mn_2O_3 as oxygen carrier since no extensive studies were found on synthesizing Malaysia bauxite waste that contains high amount of Fe with Mn_2O_3 as oxygen carrier.

2. Methodology

Bauxite waste from kuantan, Pahang was tested in this study as a Fe-based oxygen carrier. The bauxite waste was heated at 950°C for 9 hours prior dry impregnation process in order to remove the moisture content that may present in the samples and to ensure complete oxidation process. Then, the sample was crushed and sieved in order to get fine powder. After that, aqueous solution was prepared by dissolving manganese (II) nitrate with distilled water with a molarity 5.3M. Then, this aqueous solution was pipetted onto the prepared bauxite waste. Next, the sample was heated at 220°C about 24 hours for the thermal decomposition of manganese (II) nitrate to the impregnated metal oxide (Mn_2O_3). Thus, samples were calcined at different temperature, 800°C, 900°C, 1000°C and 1100°C. This research focuses on varying the temperature at more than 800°C in order to find optimum temperature for Fe-Mn when bauxite waste was used as Fe-based oxygen carrier since formation of Mn_2O_3 starts to yield at temperature more than 800°C [18].

Then, the samples were characterized for morphological, elemental and structural analysis. Morphological and elemental analysis was characterized using Scanning Electron Microscope (JEOL, JSM 6010 PLUS/LV) at magnification 100x. Meanwhile, structural characterization was analyzed using X-ray Diffraction (XRD 6000 SHIMADZU) at a scan speed 4°/min using CuKα radiation. Then, the crystallite size of powders was calculated by using Scherer equation. The Scherer equation is given below [22],

$$D = (0.9\lambda) / \beta \cos \theta \qquad (1)$$

where λ is the radiation wavelength (for CuKα radiation, λ 1.5418Å), D is crystallite size (in nm), θ is the diffraction peak angle , and β is the broadening of the line (“half width”) measured at half its maximum intensity (in radians).

3. Results and Discussions

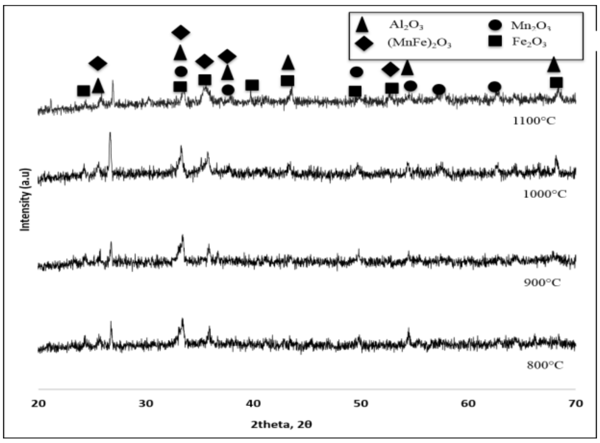

Fig. 1: XRD of bauxite waste-Mn_2O_3 at different calcination temperature

Fig. 1 shows XRD analysis of bauxite waste with Mn_2O_3 at temperature 800°C, 900°C, 1000°C and 1100°C. The presence of Fe_2O_3 and Mn_2O_3 can be observed at all temperatures corresponding to JCPDS 33-064 and JCPDS 41-1142, respectively. Cockyane et al. [18] stated that formation of Mn_2O_3 occurs at temperature above than 800°C. This XRD pattern indicates that both compositions did not undergo significant reactions and physic-chemical changes [23]. In addition, Haider et al. [17] suggested that differentiation between manganese and ferum peaks can be problematic because of their close proximity in periodic. Furthermore, natural ores or minerals have complex spectra due to minerals and impurities that present in the samples. Moreover, combination of Fe-Mn capable to increase the cycle numbers or redox reaction in CLC process hence reduces the cost to replace the oxygen carriers [17].

Meanwhile, formation of Al_2O_3 can be seen at temperature 800°C due to the presence of Al_2O_3 in bauxite waste. However, this Al_2O_3 starts to crystalline at 1000°C due to the enough heat had been presented. Since the phase changes from γ-Al_2O_3 to α-Al_2O_3 occurs at 1050°C, α-Al_2O_3 nuclei starts to nuclei at temperature above than 1000°C [24]. However, since the temperature is not high enough, α-Al_2O_3 could not grow at temperature 1000°C compared to 1100°C [25]. Nevertheless, oxygen carrier composed of Fe_2O_3 and Al_2O_3 as a binder has been proven to have high reactivity and high CO_2 yields in CLC process [26].

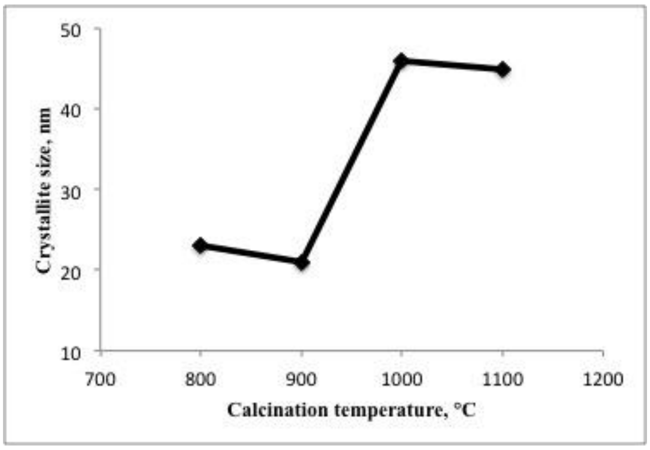

Fig. 2: Crystallite size of bauxite waste – Mn_2O_3 at different calcination temperature

Fig. 2 shows a crystallite size of bauxite waste and Mn_2O_3 when calcined at different temperature. From Fig. 2, crystallite size of the sample shows slightly decreases, 23nm to 21nm, when increases calcination temperature from 800°C to 900°C, respectively. Then, crystallite size of the samples increases, 21nm to 48nm at 900°C to 1000°C, respectively. Afterwards, the crystallite size shows slightly decreases from 1000°C to 1100°C. Increases in calcination temperature lead to the growth of crystallite size due to the heat presented that can produce larger crystallite structure. This process can be attributed to the preparation of the necessary activation energy for the growing of the crystallites at higher temperature [25]. However, the decrease of crystallite size suggests the prevention of crystal growth and improves the crystallanity of the particles at high temperature [27].

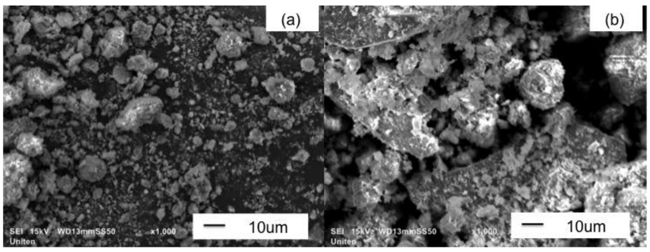

Fig. 3: Microstructure analysis of bauxite waste-Mn_2O_3 at calcination temperature a) 800°C b) 1100°C

Fig. 3 indicates microstructure analysis of bauxite waste-Mn_2O_3 at temperature 800°C and 1100°C. Particle sizes of the samples increases when increase the calcination temperature. This is in agreement with the crystallite size result shown in Fig. 2. This is due to the occurrence of agglomeration which particles tend to adhere to each other at high temperature [28]. At temperature 1100°C, particle sizes is growing due to the enough heat for the formation of crystalline structure which can be seen in Fig.1. However, based on Fig 2., smaller and stable particle size can be obtained at temperature 900°C that is favorable in CLC application due to high surface area, hence can increase CLC performance [29].

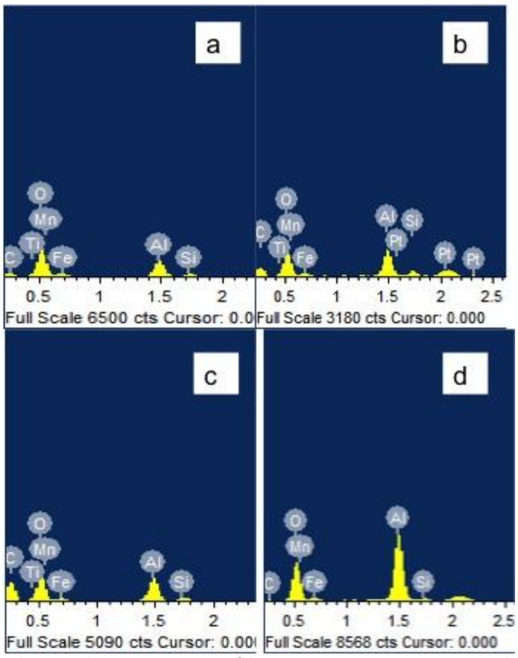

Fig. 4: Elemental compositions of bauxite waste – Mn_2O_3 at calcination temperature a) 800°C b) 900°C c) 1000°C d) 1100°C

Fig. 4 shows elemental compositions of bauxite waste-Mn_2O_3 when sintered at different temperature which were 800°C, 900°C, 1000°C and 1100°C. All elements such as Fe, Al, Mn, Si, O, C and Ti was presence at 800°C until 1100°C. Ridha et al [30] reported that presence of Ti in oxygen carrier improves the reactivity of oxygen carrier, structurally stable and have good fluidization properties. Therefore, calcination between temperature 800°C-1100°C shows a good characteristics of oxygen carrier in CLC application due to all present elements that can support to increase properties of oxygen carrier. The presence of Al_2O_3 in the bauxite waste can increase performance of CLC since it can improve the CLC performance also. Therefore, bauxite waste is a good natural resource that can be used as oxygen carrier in CLC application. The presence of Si would not affect the CLC performance [31]. Presence of C in samples was due to the carbon tape during the sample preparation and combustion process. Furthermore, presence of Pt in sample heated at 900°C due to the contamination during sample preparation. Hence, sample of bauxite waste-Mn_2O_3 at temperature 900°C is fit to be tested in a fluidized bed reactor to simulate the CLC process since it has smaller and stable particle size compared to other calcination temperature. Moreover, Ti in this sample can improve reactivity of oxygen carrier in CLC process.

4. Conclusion

According to the obtained result, Fe_2O_3 and Mn_2O_3 was successfully synthesized using bauxite waste in Malaysia. In addition, presence of Ti in sample shows the bauxite waste in Malaysia capable to increase performance of CLC. In addition, the optimum calcination temperature for Fe_2O_3 combining with Mn_2O_3 was found to be 900°C since smaller particle size can be obtained at this temperature.

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