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## Effect of MgO on characterizations and mechanical properties of red soil as oxygen carrier in chemical looping combustion

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**Abstract.** Red soil is a type of soil that rich in iron and abundantly can be found in Malaysia. However, the application of red soil is limited to agriculture, building blocks, road building and waste water treatment. Chemical looping combustion (CLC) is one of the carbon-capturing technology, in which oxygen from oxygen carrier reacts with fuel inside fuel reactor to produce pure CO<sub>2</sub> and H<sub>2</sub>O. In this research, effect of MgO as supported material was investigated in order to produce desired oxygen carrier from red soil. The composition of 95:05, 90:10, 80:20 and 70:30 of red soil and MgO, respectively, was varied in this research. The phase analysis, morphology, surface area and pore volume size were investigated using X-ray, Field Emission Scanning Electron Microscopy (FESEM) and Brunauer-Emmett-Teller (BET) analysis, respectively. From this study, composition of 90:10 of red soil and MgO, respectively, was found to have high surface area which is 56.95 m<sup>2</sup>/g with pore volume size of 0.145 cm<sup>3</sup>/g, and has low crystallite size which favourable as oxygen carrier.

### 1. Introduction

Chemical looping combustion (CLC) is carbon-capturing technology that uses oxygen from oxygen carrier to react with fuel inside fuel reactor during combustion process. The pure CO<sub>2</sub> and H<sub>2</sub>O is produced from this combustion. The reduced oxygen carrier is flow into air reactor for oxidation process and this oxidized oxygen carrier flows into fuel reactor again in order to react with fuel again. This redox reaction is repetitively occur until the oxygen carrier degrades [1]. Therefore, CLC is a promising carbon capturing technology that can capture CO<sub>2</sub> at low cost without requiring high-energy consumption and special equipment [2]. The efficiency of CLC process depends on the performance of oxygen carrier. The desired properties of oxygen carrier must have high reactivity and high regenerability during redox reaction so that replacement of oxygen carrier can be reduced, low manufacturing cost, having minimum environmental impact and resist to agglomeration with high circulation of particles during the process [3].

The Fe-based, Ni-based, Cu-based, Mn-based and Co-based are commonly metal based that used as an oxygen carrier [4]. However, Fe-based is low cost, non-hazardous, so the total operational and



manufacturing cost would be low especially using coal as fuel in CLC process [5]. However, particle agglomeration becomes major concern after several redox reactions when using Fe-based oxygen carrier [1]. Therefore, supported materials such as  $\text{Al}_2\text{O}_3$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  and YSZ were used with Fe-based oxygen carrier in order to increase the durability and performance of Fe-based oxygen carrier [6]. B.S. Kwak et al. [4] found that the  $\text{MgO}$  is stable and well resist at high temperature as the supported material.

Moreover, low cost materials were used continuously in CLC especially using coal as fuel so that replacing the used oxygen carrier would not be an issue especially from economical aspect [7]. Iron ore and ilmenite ore [8] were used continuously as Fe-based oxygen carrier from natural resources in CLC due to its properties similar to as synthesized oxygen carrier. However, most of these ores in form of rock and pretreatment is needed to be transformed into the powder. Hence, it would increase operational cost. Therefore, red soil is introduced as Fe-based oxygen carrier since it has iron oxide ( $\text{Fe}_2\text{O}_3$ ) content and in a form of soil. According to Latifi et al. [9], the properties of red soil in Malaysia contains high surface area, and high crushing strength that is very useful as oxygen carrier.

There were many methods to produce oxygen carrier such as ball milling, freeze granulation, gel combustion, and sol gel method [10-12]. However, dry impregnation method was found to be a method that can improve the chemical reactivity and mechanical properties of oxygen carrier [13]. This research was investigating the effect of composition of  $\text{MgO}$  as supported material when using red soil as oxygen carrier since few studies were found using red soil as oxygen carrier. This research used dry impregnation method during synthesization process of the oxygen carrier for CLC application.

## 2. Methodology

Red soil from Kuantan Pahang and magnesium nitrate from Sigma Aldrich were used in this research as a raw material using dry impregnation method. Red soil was dried in oven at temperature  $100^\circ\text{C}$  for 24 hours in order to remove the moisture content that may present in the red soil. Then, the red soil was sieved to the fine particle size which was less than 1 mm. After that, nitrate solution was prepared by dissolving the magnesium nitrate into distilled water in order to get the nitrate solution. Then, the magnesium nitrate solution was pipetted into the red soil at different composition which were 95:5, 90:10, 80:20 and 70:30 of red soil and magnesium nitrate solution, respectively. These compositions were chosen as limited study was found on the effect of  $\text{MgO}$  composition as supported material for red soil [14]. After that, the samples were mixed and stirred prior to calcination inside muffle furnace at  $220^\circ\text{C}$  for 10 hours. This process was done in order to reach thermal decomposition of the magnesium nitrate into magnesium oxide,  $\text{MgO}$ . Afterward, the samples were re-calcined at temperature  $950^\circ\text{C}$  for 10 hours in order to produce samples of full-oxidized red soil that impregnated with  $\text{MgO}$ .

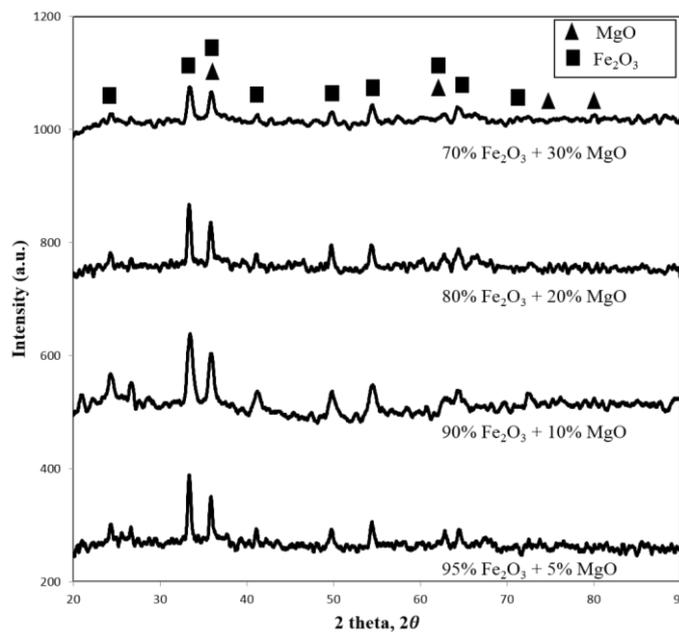
Morphology of samples were characterized using Field Emission Electron Microscopy (FESEM, HITACHI SU8030). Meanwhile the phase analysis and compositions were characterized using X-Ray Diffraction (XRD) analysis using SHIMADZU 6000. The crystalline sizes of the particles were calculated using Scherrer equation as shown below [15].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where,  $D$  is crystallite size (in nm),  $k$  is machine constant which is 0.916,  $\lambda$  is radiation wavelength which is  $\text{Cu K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ),  $\beta$  is full width at half maximum (FWHM) and  $\theta$  is the angle of diffraction peak. The full width at half maximum and angle of diffraction peak are should be converted into radians. Then, density of the samples were measured using Archimedes principle. The surface area and pore volume size were measured using BET analysis at degassing temperature  $300^\circ\text{C}$  for about 1 hour. Moreover, the particle size was analysed using image J analysis.

### 3. Results and discussions

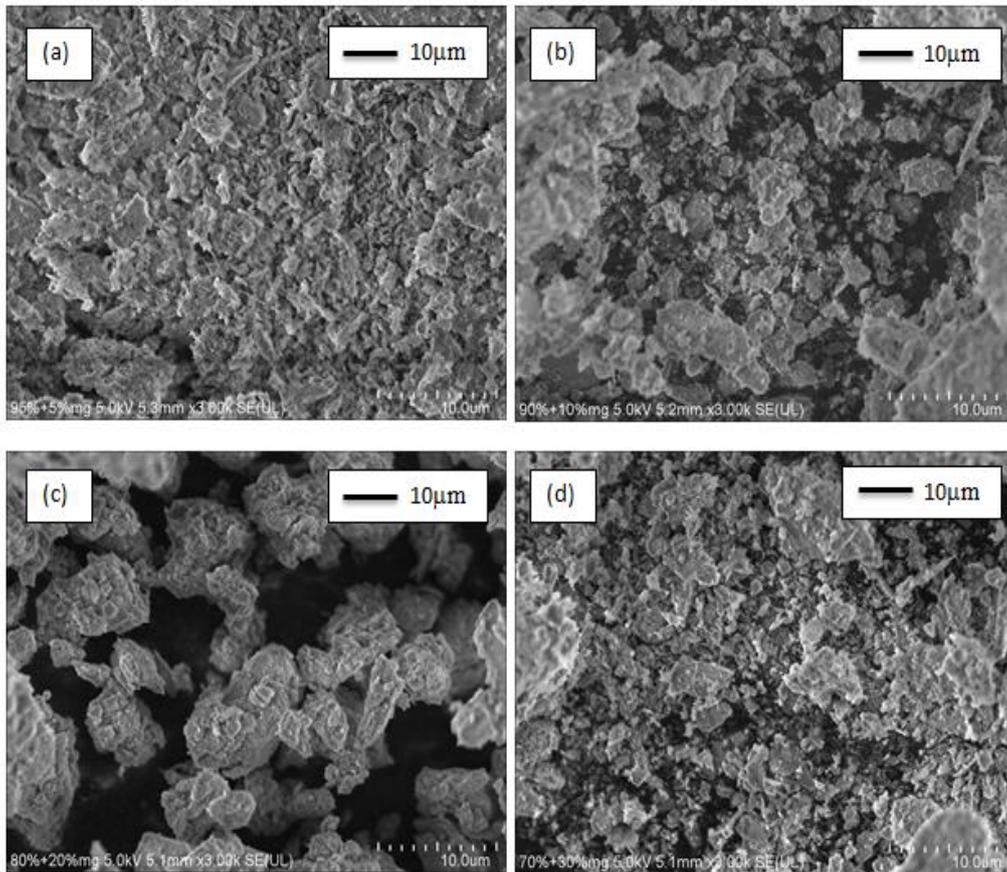
Figure 1 shows XRD result for various compositions of red soil that contains  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  with the composition of 95:5, 90:10, 80:20 and 70:30, respectively. The  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  peaks can be observed at all compositions, which correspond to rhombohedral phase of hematite  $\alpha\text{-Fe}_2\text{O}_3$ , JCPDS 33-0664 and  $\text{MgO}$ , JCPDS 78-0430, respectively. The characteristic peaks of  $\text{Fe}_2\text{O}_3$  reduce with the increase of  $\text{MgO}$  due to the amount of  $\text{Fe}_2\text{O}_3$  existed in samples decreased when  $\text{MgO}$  content is increased. This result is in agreement with Zhu et al. [16]. The peak at composition of 90:10 of red soil and  $\text{MgO}$  shows that this sample produces small crystallite size which was calculated using Scherrer equation stated in Table 1. The differences in crystallite size and crystallization could be mainly attributed to the addition of  $\text{MgO}$  in the red soil. Table 1 shows the crystallite size of various compositions of red soil and  $\text{MgO}$ . Increase the amount of  $\text{MgO}$  to the 10 % causes decrease of crystallite size. The crystallite size of compositions 90:10 shows the smallest crystallite size which is 113 nm. This is due to the possibility of surface segregation of  $\text{MgO}$  with  $\text{Fe}_2\text{O}_3$  that leads to the decrease in surface energy hence decreases in particle size [17].



**Figure 1.** XRD analysis of  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$ .

**Table 1.** Properties of various compositions of samples.

Percentage ratio of $\text{Fe}_2\text{O}_3$ and $\text{MgO}$ (%)	Crystallite size (nm)	Density ( $\text{g}/\text{cm}^3$ )	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )
95% + 5%	198	1.90	36.54	0.128
90% + 10%	113	1.86	56.95	0.145
80% + 20%	181	1.88	34.83	0.123
70% + 30%	130	1.83	41.76	0.122



**Figure 2.** Morphology of various compositions of Fe<sub>2</sub>O<sub>3</sub> and MgO (a) 95:05 (b) 90:10 (c) 80:20 and (d) 70:30.

Figure 2 shows the morphology analysis of four samples that tested by field emission scanning electron microscopy (FESEM). The Figure 2(a), 2(b), 2(c) and 2(d) shows the composition of 95:05, 90:10, 80:20 and 70:30 of Fe<sub>2</sub>O<sub>3</sub> and MgO, respectively. The Figure 2(a) shows that the particles are in irregular shape and have flaky morphology probably due to the breaking of agglomeration of iron oxide. This can be attributed to the amount of MgO added in Fe<sub>2</sub>O<sub>3</sub> that causes the breaking of iron oxide. The Figure 2(b) revealed that the flaky morphology presents in the samples too. In Figure 2(c), the agglomeration starts to form bigger particle size and has irregular in shape. Whereas, the figure 2(d) shows that, the particle size starts to break into small particle size. The particle size in the sample of 80:20 of red soil and MgO, respectively, is larger compared to other compositions. It clearly can be seen in Figure 3 that shows the particle size distribution of samples at various compositions. So, the sample powder of 90:10 can react better than other compositions since it has high surface area hence increase reactivity of samples [18].

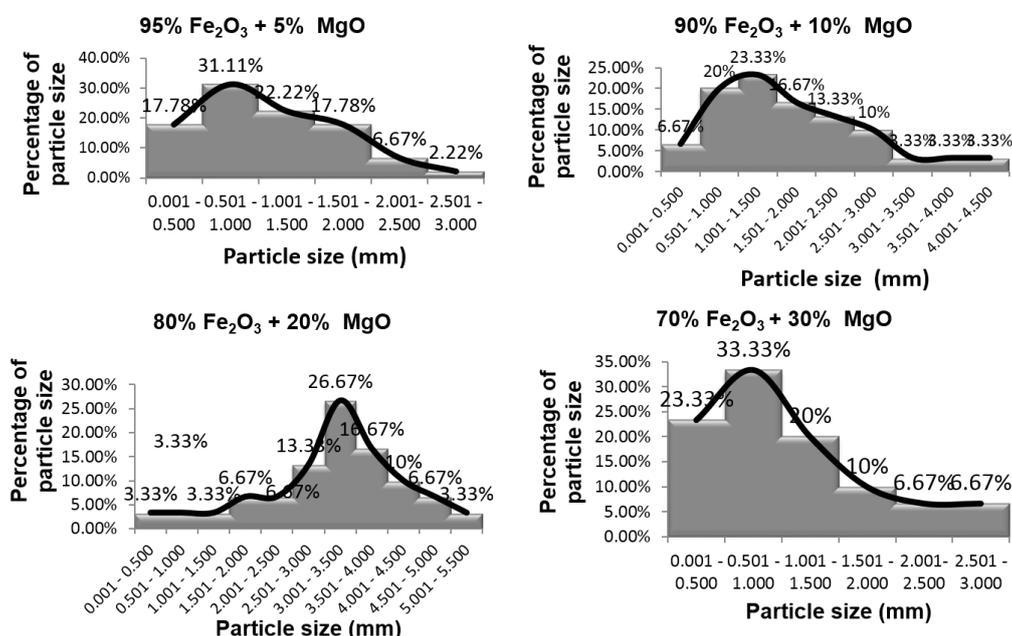


Figure 3. Particle size distribution of samples at various compositions.

In addition, density of samples at composition of 95:5, 90:10, 80:20 and 70:30 of Fe<sub>2</sub>O<sub>3</sub> and MgO, respectively, are in between 1.80 g/cm<sup>3</sup> to 1.90 g/cm<sup>3</sup> as shown in Table 1. The densities of these samples are within the density range of good oxygen carrier for CLC which is in between 1.50 g/cm<sup>3</sup> to 4.00 g/cm<sup>3</sup> [19]. However, the composition of 90:10 of red soil and MgO, respectively, has higher surface area than other composition, which is 56.95 m<sup>2</sup>/g as shown in Table 1. This is due to the possibility of surface segregation of MgO with Fe<sub>2</sub>O<sub>3</sub> that leads to the decrease in surface energy hence decreases in particle size [17]. Higher surface area can increase the reactivity of oxygen carrier [20]. Therefore, 90:10 shows good mechanical properties since it has higher surface area, appropriate density and lowest crystallite size.

#### 4. Conclusions

In this research, effect of the composition of MgO was investigated when using red soil as oxygen carrier. From this research, it was found that composition of 90:10 of red soil and MgO, respectively, has high surface area and pore volume size, and low crystallite size. Hence, the 90:10 composition of red soil and MgO, respectively, can be analysed using the TGA and fluidised bed reactor in order to simulate the CLC condition. Moreover, the composition of MgO can affect the properties such as surface area and morphology of oxygen carrier.

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