Effect of Calcination Time on Physical and Chemical Properties of CaO- catalyst Derived from Industrial-eggshell Wastes

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Abstract

In this study, eggshell wastes from a hatchery industrial plant were carefully-calcined under air-atmosphere at 800 ºC in the range of 1 to 4 hours. Then both physical and chemical properties of calcium oxide derived from calcination of eggshell wastes were systematically characterized by XRF, XRD, SEM, particle size analyzer and gas adsorption experiment. The XRF results and the XRD patterns indicate that all calcination times completely transformed the eggshell wastes to be a crystalline calcium oxide phase with about 98 % w purity of calcium oxide. The SEM characterization results indicate rod-liked porous surface on the obtained calcium oxide and size of surface pore are slightly increased with increasing of calcination times. The Langmuir surface area of the obtained calcium oxides was determined by N_2 adsorption experiment at -195 °C. This experiment showed that the surface area of the obtained calcium oxides is rapidly decreased from 14.9 to 2.0 m^2/g with increasing of calcination times from 1 to 4 hour. These results indicate that calcination time is one of the factors determining both physical and chemical properties of calcium oxide. Additionally, this present study also provides a new optimum condition to produce calcium oxide from industrial-eggshell wastes with both physical and chemical properties comparable to commercial calcium oxide.

Keywords: Calcium oxide, Catalyst, Eggshell

Introduction

In Thailand, large hatchery farms generate eggshell wastes (about 6.6 tons per annum) and this waste normally goes to landfill site. This waste management scheme leads to several environmental concerns e.g. landfill leachate, odor and methane emission from landfill. Furthermore, landfill site normally cause a crucial conflict between hatchery farms and their neighbors. So, large amount of eggshell wastes have to be managed properly. Recently, eggshell has been extensively studied as a starting material for preparing low-cost calcium oxide. This is because calcium oxide is normally used as an environmentally-friendly heterogeneous catalyst in a wide range of processes, e.g. chemical synthesis, petrochemical industry and biodiesel production process. In addition, calcium oxide can be separated from product and can be regenerated\reused in several cycles of production process. Currently, researchers reported that high purity of calcium oxide can be produced from eggshells due to it contain with high content of $CaCO_3$. Thermal decomposition of eggshell above 700 °C is a facile method to decompose eggshell in to carbon dioxide and calcium oxide. Several synthesis conditions on thermal decomposition of eggshell at different temperatures and under different atmospheric conditions were reported. However, the effect of calcination time on surface properties of

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calcium oxide has not been clearly reported. In this work, the effect of calcination time on physical and chemical properties of CaO-catalyst derived from Industrial-Eggshell wastes was investigated in order to find the optimum condition to produce calcium oxide from industrial-eggshell wastes.

Experimental

1. Raw Material

Chicken eggshell wastes used in this study was obtained from one of the largest hatchery farms in Nakon Ratchasima province, Thailand. The eggshell wastes were rinsed with water to remove dirt and other impurities and were dried in an oven at 105 ºC for 24 hour. The egg-shell membranes were separated manually. Then, the eggshell wastes were crushed in to powder with Panasonic MX-AC400 crushing machine followed by screening through a set of sieves to get a grain size lower than 425 micrometer.

2. Sample Preparation and Characterization

Calcium Oxides (CaO) were prepared by a thermal decomposition method. The eggshell powders were calcined in muffle furnace from room temperature to 800 °C with a heating rate of 50 °C/min. Furnace temperature was maintained at 800 °C for 1 to 4 hour under air atmosphere. Then, the furnace was left to cool down to 120 °C before calcined eggshell wastes were taken to desiccator. All calcined eggshell samples were kept in the vacuum desiccator to avoid the sample reacting with moisture and carbon dioxide in the atmosphere. Crystal structures and elemental composition of the calcined eggshells were determined by X-ray diffractometer (XRD – PW 3040/60 X'PERT PRO Console) with Cu-K radiation and X-ray fluorescence analyzer (XRF-Bruker S4 Explorer), respectively. Surface morphology of calcined eggshells were investigated by scanning electron microscopy (SEM – LEO 1455VP). Particle size diameter of the samples was analyzed by laser diffraction particle size analyzers (Beckman Coulter LS 230). In addition, Langmuir surface area of the samples was measured by N_2 adsorption/desorption isotherm at -195 °C (Micro meritics-TriStar II 3020).

Results and Discussions

1. Effect of calcination time on chemical properties of CaO derived from industrial- eggshell waste

XRD patterns and their major peaks of both calcined eggshells from various temperatures and commercial calcium carbonate are presented in (Figure 1) and (Table 1), respectively. The XRD pattern of commercial calcium oxide match with peak data collected from Joint Committee on Powder Diffraction Standards (JCPDS). This indicated that crystal phase of commercial calcium oxide is in both calcite and aragonite form. The XRD patterns and peaks obtained from calcined eggshells are similar to calcium oxide data collected by JCPDS. The results of XRF showed that CaO was the most abundant component in eggshell wastes (68.2 % w). (Table 2) shows the eggshell wastes also contained small amounts of Mg, P_2O_5, Na_2O, SO_3, and K_2O. However, high purity of CaO (about 98.0 % w) can be obtained after eggshell wastes were calcined at 800 °C at various times. Both XRD and XRF results showed that calcined eggshells at 800 °C from 1 to 4 hour, thermally decomposed calcium carbonate in eggshells to carbon dioxide and calcium oxide.

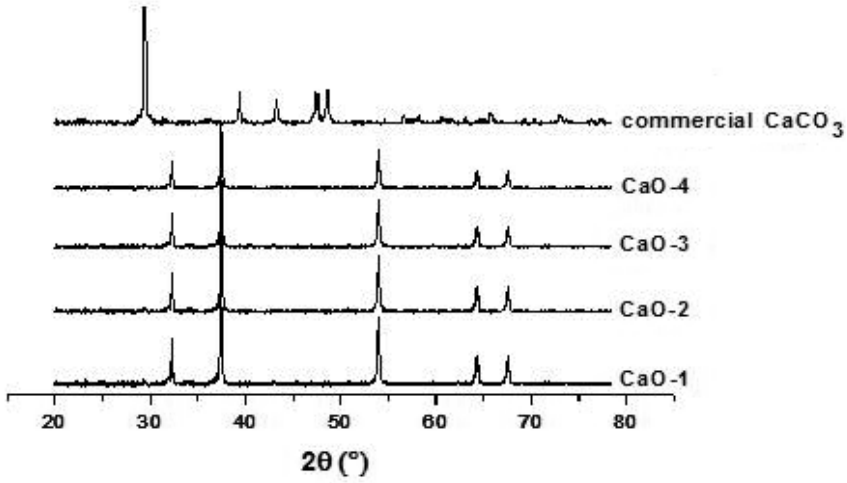

Figure 1 XRD patterns of commercial $CaCO_3$ and calcined eggshell waste at 800 ˚C for 1 to 4 hr

Table 1 Major diffraction peaks of commercial CaO and calcined eggshell waste collected by XRD technique.

Sample	Decomposition temperature	Compound	2θ
JCPDS data [1]	-	$CaCO_3$	29.4° 39.4° 43.2° 47.4° 48.5°
		CaO	32.2° 37.3° 58.3° 64.1° 67.3°
Egg-shell wastes[2]	800 °C 2h	CaO	32.3° 37.42° 53.92° 64.22° 67.42°
Egg-shell wastes	As received	$CaCO_3$	29.4° 39.5° 43.2° 47.6° 48.6°
(this study)	800 °C 1h	CaO	32.2° 37.4° 53.9° 64.2° 67.4°
	800 °C 2h	CaO	32.2° 37.4° 53.9° 64.2° 67.4°
	800 °C 3h	CaO	32.2° 37.4° 53.9° 64.2° 67.4°
	800 °C 4h	CaO	32.2° 37.4° 53.9° 64.2° 67.4°

Table 2 Chemical composition of the samples determined by X-ray fluorescence spectrophotometer.

Element (%w)	CaO-1	CaO-2	CaO-3	CaO-4	CaO [3]	Eggshell
CaO	97.9	98.0	97.9	97.9	97.42	68.2
MgO	0.977	0.984	1.01	1.01	1.63	0.459
P_2O_5	0.543	0.530	0.579	0.532	0.52	0.396
Na_2O	0.223	0.162	0.171	0.161	-	0.103
SO_3	0.111	0.107	0.116	0.120	0.26	0.105
K_2O	0.065	0.034	0.045	0.036	0.08	0.0622

2. Effect of calcination time on physical properties of CaO derived from industrial-eggshell wastes

(Figure 2-3) shows SEM photographs of eggshell and calcined eggshell wastes, respectively. It expressed the rough surface of eggshell with some small pores while calcined eggshell waste obtained from different calcination times showed similar micromorphology of rod-liked or dumbbell shaped. This rod-liked shape occurred during thermal decomposition of carbonate contained in eggshell

and this rod-liked shape possibly provides higher surface area than original eggshell waste.

Particle size diameter of the samples is shown in (Figure 4). Initially, particle size diameter of crushed eggshell waste was about 248.4 micron but particle size diameter of the sample gradually reduced to 59.82, 13.43, 13.75, 12.87 micron for CaO-1 to CaO-4, respectively. This indicated that particle size diameter of the sample decreased with increasing of calcination time.

The Langmuir surface areas of CaO derived from different calcination time were shown in (Figure 5). It appeared that surface area of the sample significantly increased about 5.7 times after the eggshell sample was calcined at 800 °C for 1 hour. However, the surface area of the calcined samples significantly decreased from 14.9 m^2/g to 2.0 m^2/g with increasing calcination time from 1 to 4 hour. Additionally, the surface area of calcined eggshell waste at 800 °C for 1 hour is remarkably higher than surface area of commercial calcium oxide.[4]

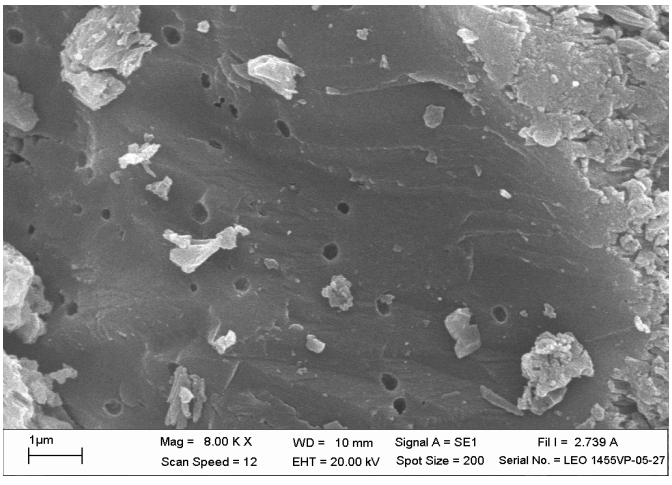

Figure 2 SEM photograph of eggshell waste with 8,000x magnification.

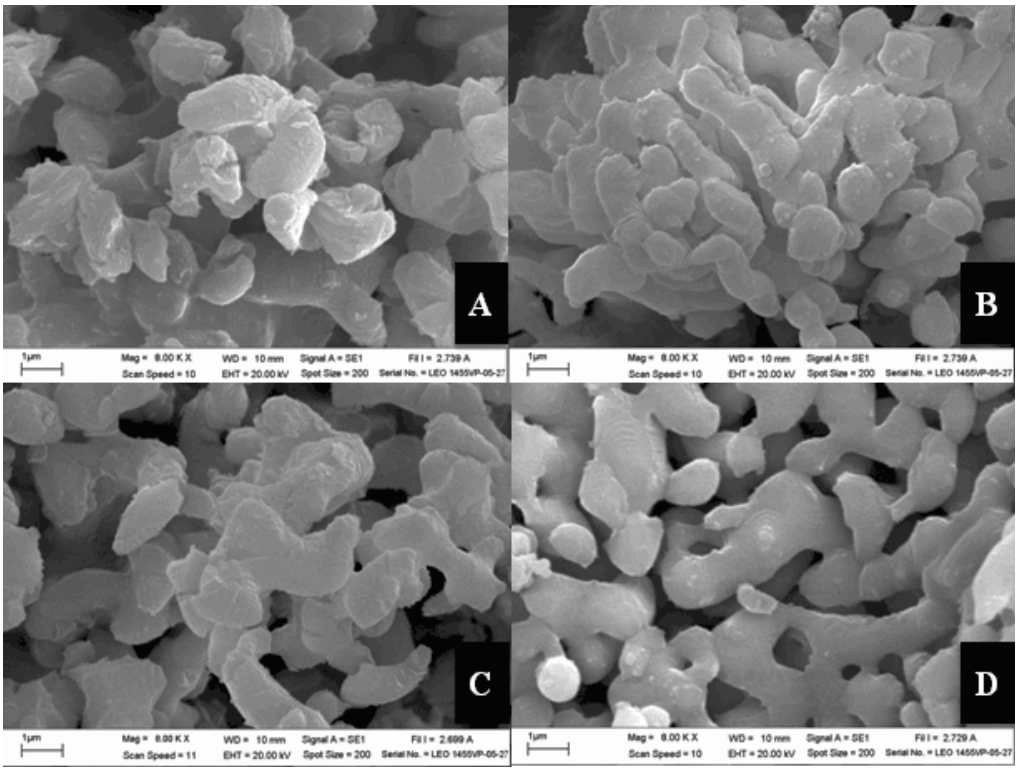

Figure 3 SEM photographs of calcined eggshell wastes at 800 °C for 1 to 4 h with 8,000x magnification, CaO-1 (A), CaO-2 (B), CaO-3 (C) and CaO-4 (D)

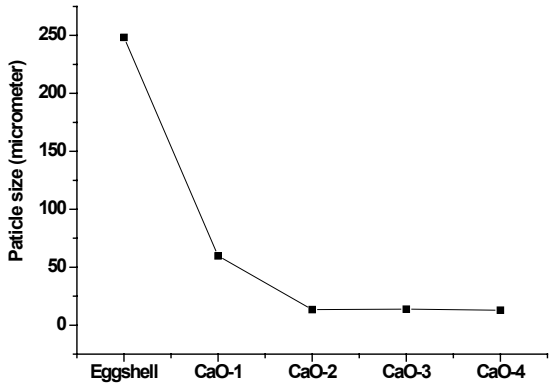

Figure 4 Particle size diameter of samples obtained from various calcination conditions.

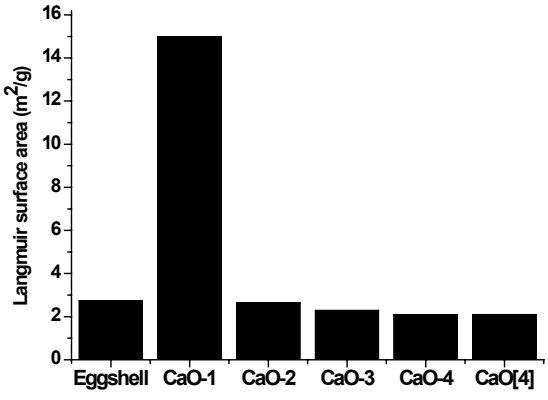

Figure 5 Langmuir surface area of various samples.

Conclusion

In this work, effect of different calcination times on both chemical and physical characteristics of calcium dioxide derived from eggshell wastes was reported. The results indicated that both particle size and surface area decrease with increasing calcination time. In terms of energy conservation, calcination of industrial-eggshell wastes at 800 ºC for 1 hour is enough to produce high purity of calcium oxide. In addition, high surface area of calcium oxide can also obtained at this optimum calcination temperature and time. This study also indicated that both physical and chemical properties of calcium oxide obtained from eggshell waste were comparable to commercial calcium oxide.

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