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Original Research Paper

Study on the Properties of Calcined Waste Mussel Shell

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ABSTRACT

Mussel shell has been calcined on high temperature. Its main component calcium carbonate is decomposed into CO_2 and calcium oxide. Calcium oxide is superbase catalyst for the transesterification reaction. By means of differential thermal balance, the decomposition characteristics of mussel shell have been studied. And of electron microscope, TEM shows grain morphology characteristics of calcination at different calcining temperatures. Organic matter has decomposed during 287°C-458°C. Decomposition of calcium carbonate starts from 600°C to 800°C, when it was balanced. By use of orthogonal analysis, the main influence factors of specific surface area have been optimized. The optimal process parameters are 950°C calcination temperature, 120ì m initial diameter and 1 hour holding time.

INTRODUCTION

In recent years, the market scale of pearl jewellery promoted the rapid development of mussel farming. Annual production of mussel shell is over one million tons, and most of them are discarded as wastes in mussel farming area to cause serious pollution of the local water environment. So it is urgent to solve the environmental problems. The main component of mussel included more than 95% $CaCO_3$, a small number of shells hormone (organic matter and trace elements) and a small amount of K, Na, Zn, Sr, Fe, Mg, etc. Furthermore, the Mussel shell contains no sulphur (Pokroy 2004). By firing mussel shell, higher degree of alkali reactive solid super base calcium oxide has been obtained, which can be used directly to the catalytic bio-diesel production. The decomposition product of the mussel shell contains a small amount of zinc oxide and strontium oxide which can improve the activity of calcium oxide alkali (Takahashi 2004). This method not only made the abandoned mussel shell into treasure but also played the role of the environmental protection. So the preparation of highly active calcium oxide has broad application prospects from mussel shell (Vicente Gemma 2004) .

The decisive factor of the catalytic activity of solid calcium oxide as super base catalyst is specific surface area (Nobutake & Bai 2009). The size of mussel shell and specific surface area are closely related to the production process, including the particle size of the raw materials (Hattori 2001), the calcined temperature and the keeping time (up to a certain temperature after the thermostat time). Currently, the research of shell is focused on the desulfurization performance, the microstructure and thermodynamic properties, etc.

In this paper, by means of electron microscopy, the change of calcinated surface area can be scanned under different temperatures. The quality and thermal stability of river mussel shells can be learnt by differential thermal balance. The optimal production conditions of catalyst can be received by orthogonal experiment method.

MATERIALS AND METHODS

Five age living mussels in Nanyang Ap River reservoir were selected as the object of the study. Firstly, meat on the mussel shell surface must be stripped away and be washed with tap water, then sediment and other impurities attached to the surface were removed by steel brush. Secondly, the mussel shells were soaked for two hours with 0.01% sodium hypochlorite solution then washed with tap water and steel brush. They were further soaked for 0.5 hours with 0.5% hydrochloric acid (Serio 2008). At last, the shells have been washed four times with distilled water to remove a variety of organic and inorganic impurities present on the surface. They were kept in a constant temperature oven at 105°C for drying for one hour, crushed, and sieved through 60 mesh, 80 mesh, 100 mesh and 120 mesh to obtain the particle diameter of about 250μm, 180μm, 150μm and 120μm.

Thermal decomposition principle of mussel shell is as follows:

$$CaCO_3 \overset{\Delta}{\rightleftharpoons} CaO + CO_2 \qquad ...1$$

The transient analysis curves of DTA and TG when mussel shell is decomposed are based on differential thermal balance LCT-2B. 20mg different size shell powder was taken as thermal analysis samples. Parameters have been set: sam-

pling interval as 1000ms, uniform temperature as 5°C per minute, and the final temperature is set to 1100°C. Because calcium oxide can be poisoned easily by carbon dioxide and water vapour in the air, the reaction should be carried out under the protection of nitrogen. Mechanism of calcium oxide being poisoned is following:

$$CaO + CO_2 \bullet CaCO_3 \quad ...2$$
$$CaO + H_2O \bullet Ca(OH)_2$$

Shell powder treated with alumina crucible in a muffle furnace as 10°C per minute uniform temperature to 800°C, 950°C, 1000°C or 1100°C (constant calcined temperature). Hitachi S-3400N-a type scanning electron microscopy was used to observe the morphology of the calcined product of different temperature. Specific surface area of product was measured by low temperature nitrogen adsorption method (BET). Absorbed-bate used nitrogen, relative pressure is set to 0.15MPa and temperature was set at 180°C (nitrogen liquefaction point is -195°C), thus chemical adsorption can be avoided under low temperature.

Determination of the specific surface area generated was made by BET (discovered by three scientists Brunauer, Emmett and Teller). Specific surface area refers to the total surface area per gram of powder, particulate lattice outer surface area and crystal lattice empty cavity surface area superimposed, namely low-temperature adsorption. The theoretical basis was that the gas was absorbed in the surface porosity of particles. Under conditions of constant temperature and equilibrium state, the solid surface has a certain amount of adsorption of a certain pressure gas. The gas pressure determines the amount of adsorbed material.

This method is currently recognized as the standard method for the measurement of solid surface area. The measurement principle is that physical adsorption would occur in the surface of the material (grain interior and the surface of the external through hole) at low temperature. The physical adsorption is based on multilayer approach, the first layer is not yet saturated, adsorption to produce a second layer on which the adsorption takes place. They may produce a second layer on the third layer adsorption; the adsorption equilibrium stability layers adsorption reached equilibrium at the same time. The measurement of gas adsorption pressure and the adsorption volume can be calculated, and so the specific surface area. Isotherm equation is given in formula (3):

$$\frac{P/P_0}{V(1-P/P_0)} = \frac{C-1}{V_m C} \times P/P_0 + \frac{1}{V_m C} \quad ...3$$

Where V is volume of gas adsorption (unit is millilitre), V_m is monolayer saturation adsorption capacity, P is the adsorption pressure/Pa, P_0 is the adsorption saturated vapour pressure/ Pa and C is the coefficient.

Here, let:

$$Y = \frac{P/P_0}{V(1-P/P_0)} \qquad X = P/P_0$$

$$A = \frac{C-1}{V_m C} \qquad B = \frac{1}{V_m C}$$

According to the experimental measurements, drawing the curve of $Y = AX + B$.

So the value of V_m was obtained. The surface area can be obtained by formula (4).

$$S_g = \frac{4.36 \times V_m}{W} \quad ...4$$

RESULTS AND ANALYSIS

Decomposition characteristics and morphology of the mussel: DAT and TG curves (Fig. 1) show the mussel shell decomposition process, in the range of 287°C to 458°C, accompanied by a strong exothermic peak and with weightlessness weight loss rate of 4.1%, which is presumably because of the decomposition of organic matter and released heat. There was one slight weaken exothermic peak in the

Table1. Factors and levels of specific surface area.

Levels	Diameter/μm (A)	temperature/°C (B)	Holding time/h (C)
1	120	800	0.5
2	150	950	1
3	180	1000	1.5
4	250	1100	2

Table 2: Orthogonal analysis of calcined product.

No	Factors			Average specific surface area/m^2/g
	A	B	C	
1	1	1	1	31.2
2	1	2	2	42.5
3	1	3	3	51.9
4	1	4	4	36.5
5	2	1	2	27.5
6	2	2	1	38.5
7	2	3	4	36.9
8	2	4	3	29.3
9	3	1	3	30.3
10	3	2	4	43.3
11	3	3	1	37.4
12	3	4	2	40.1
13	4	1	4	31.1
14	4	2	3	33.2
15	4	3	2	34.3

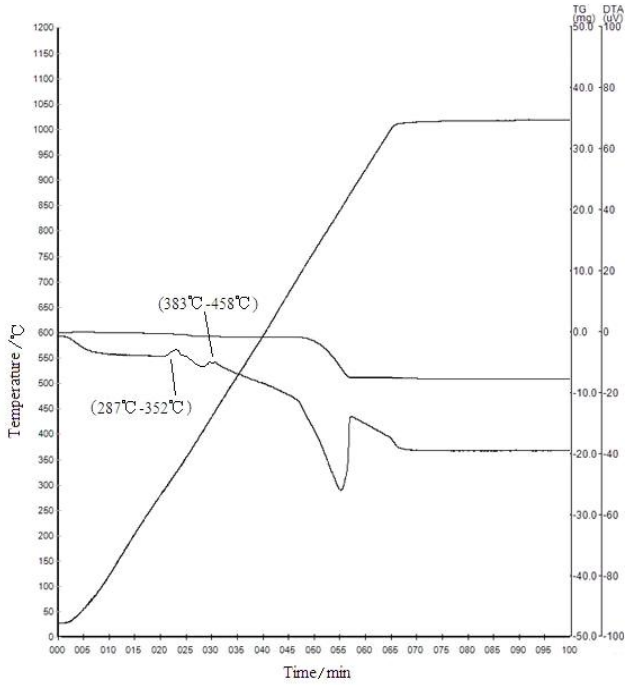

Fig. 1: Thermal analysis spectra of mussel shell.

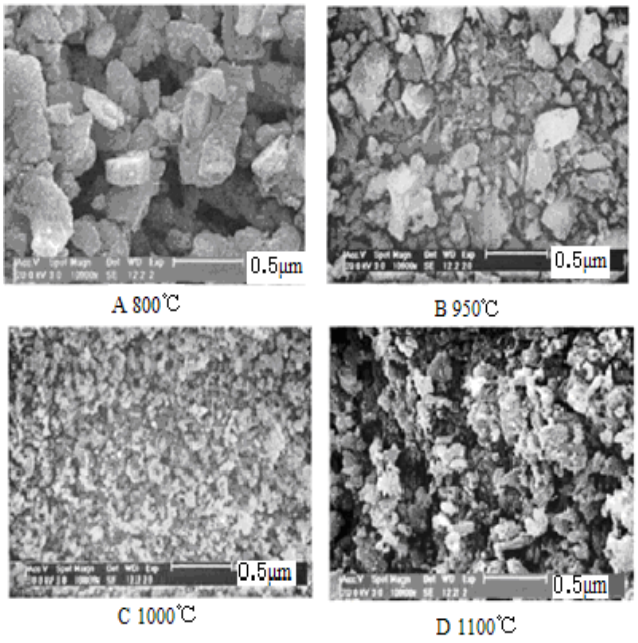

Fig .2: Scanning electron microscope image of mussel shell calcinations at different temperatures.

range of 383°C to 458°C of the calcium carbonate crystal phase transition from aragonite calcite phase caused by the endothermic weakening of the role in the exothermic decomposition of organic matter. Calcium carbonate decomposition occurs when the temperature rose during 600°C to 800°C, and at the same time, rapid weight loss and more endothermic phenomenon accounted that mussel shell main ingredients generated calcium oxide and CO_2 (Zhang 2011).

As weight loss rate is known, it can be found that mussel shell contains about 94.875% of the calcium carbonate. The sample of decomposition was dissolved with 1% hydrochloric acid and titrated with 5% sodium carbonate solution, then dried in addition. Calculated production showed that mussel shell contains about 94.68% of calcium carbonate. When the calcined temperature reached 900°C, TG curve does not change, and the decomposition of calcium carbonate reached equilibrium (almost completely decomposition). With continuing heating, another period of endothermic generated when lattice defect of calcium oxide gradually reduced. At 1100°C, calcium oxide turned into molten sintering as shown in Fig. 2-D. The TEM images (Fig. 2) of the sample show the product as calcined at different temperatures to 120 mesh and the particle size of mussel product gradually refined as the temperature increased.

Powder diffractometer was used to verify the composition of the calcined product. Copper was used as the medium. Detecting results are shown in Fig. 3. Strong diffraction peak was coincident to that of calcium oxide. It can be seen from the diffraction pattern of the calcined product that calcium carbonate is disappeared. Those weak peaks at 100, 102 and 110 represent zinc oxide.

Specific surface area of orthogonal design: The specific surface area of the catalyst particles determines the efficiency of heterogeneous catalyst. Therefore, the orthogonal design method of calcined product was chosen to study the main factors affecting the specific surface area. The main factors were pulverized particle diameter R (A), the calcined temperature θ (B) and the holding time *t* (C), each with four levels, and average value thereof. Factors and levels are given in Table 1.

In accordance with the requirements of the orthogonal design, strict test was arranged in a combination of factors, and the experimental program and test results are given in Table 2.

As can be seen from the analysis results, the calcined temperature is the most important factor on the contrast surface area; the initial crushing particle size is more and the holding time is important yet. The calcium carbonate decomposition is a reversible reaction, the higher the temperature, the faster and thorough is decomposition, so the particle is refined more rapidly. There was certain lattice distortion among the grains of calcium oxide. As the temperature continues to rise, the lattice atoms reconstruction reduced the gap among each other, thereby reducing the

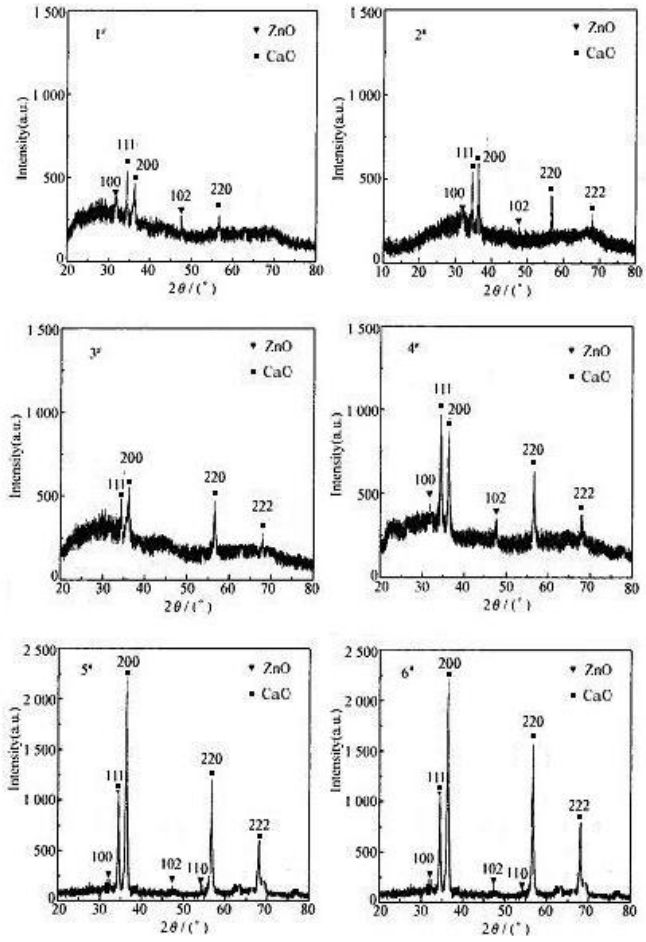

Fig .3: XRD pattern of calcined product.

specific surface area of the product. So when the temperature was at 1000°C, the product particles reach nanometer level, close to 50nm. Decomposition of the calcium carbonate was from outside to inside, so smaller the particle the more easily was decomposition, and it can easily reach the balanced decomposition. Holding time played a certain role on the lattice reconstruction of decomposition products, while their impact is relatively minor comparing to the calcined temperature.

Specific surface area reached maximum only when the original particle size was 120μm, calcining temperature 1000°C and holding time one hour. Therefore, from Table 2, the best process of largest specific surface area was B3A1C2. Calcined mussel in accordance with this condition, obtained heterogeneous catalytic 42.53m^2/g, and a higher rate of transesterification obtained when it was applied to the production of bio-diesel. So it fully meets the requirements of catalytic superbase catalysts.

CONCLUSION

1. The differential thermal analysis of the mussel shell discovered its thermal decomposition rule that which two significant changes have occurred in uniform during the heating process. From the DAT and TG curve of mussel shell, the decomposition of organic and calcium carbonate have generated with the loss of shell weight. Calcium carbonate content can be calculated about 94.68%. DAT curve becomes less steep when the temperature rose to 800°C, while calcium carbonate is almost completely decomposed.
2. TEM image shows that a small amount of mussel decomposed when the temperature was at 600°C. As the calcined temperature raised, the calcination becomes smaller and smaller. The product gradually molten and sintering when the temperature is at 1100°C.
3. By orthogonal experimental design, calcined temperature was the most important factor in the three factors. Production conditions of the calcined temperature of 950°C, the initial particle size of 120μm and the holding time of one hour were perfect to obtain the optimum surface area of calcination.

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