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Meso-porosity and phase transformation of bird eggshells via pyrolysis

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Bird eggshells have fascinated mankind for centuries because bird egg is one of the most nutritious foods consisting of protein, lipid, and carbohydrates. Bird eggs also contain vitamins and mineral elements that are necessary for the development of young and elderly people. Phase transformation of bird eggshells was investigated here quantitatively and qualitatively through an analysis by XRD. Most of raw bird eggshells show calcite ($CaCO_3$) of the rhombohedral form at nearly 100 wt % and it changed to lime or calcium oxide (CaO) of the face-centered cubic form at 97.41 wt % mixed with a small amount of other oxide compounds such as MgO and $Ca(OH)_2$ when the bird eggshells were calcined at 900 °C for 1 h. The calcium oxide had a N_2 adsorption-desorption isotherm expressed as the type IV hysteresis loop and a small average pore diameter in the range of the meso-porosity. Furthermore, the samples were analyzed by FTIR, STA, XRF, TEM, BET, and a particle size analyzer. The calcined bird eggshell powder is potentially useful for a variety of applications and industries: ink; fertilizer; cosmetic; pharmaceutical; rubber; plastic, including acting as starting materials for gypsum and dielectric-magnetic materials.

Key words: Bird eggshells, Phase transformation, Meso-porosity, Pyrolysis.

Introduction

Bird eggs are a famous food and a most important ingredient which provids protein. Most people toss broken eggshells right into the garbage. Egg and egg derivative consumption produce a great amount of shells and their wastes constitute an environmental problem and a part of the global warming climate problem. In general, the main functions of the eggshells are for protection, and gas and water exchange [1]. They also provide the embryo with minerals, primarily calcium, needed for the developments of high-calcium consuming organs such as the skeleton, muscle and brain [1]. Bird eggshell typically consists of ceramic materials or inorganic compounds constituted by a three-layer structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer. The spongy and mammillary layers form a matrix composed of protein fibers bonded to calcite (calcium carbonate) crystal. The two layers are also constructed in such a manner that there are numerous circular openings (pores) to permit gaseous exchange throughout the shell. The outer surface of the eggshell is covered with a mucin protein that acts as a soluble plug for the pores in the shell. The cuticle is also permeable to gas transmission [2]. Eggshell porosity is determined by three factors: the number of pores, their individual cross-sectional area and their length. One mechanism for the control of shell porosity may lie in the number of seeding sites upon which shell calcification is initiated. These sites determine the number of crystal columns in the shell which in turn are positively correlated with the number of pores [3]. The number of columns in a unit area of the shell is inversely proportional to the shell thickness, i.e. the pore length and may also determine the individual cross-sectional area of the pores [3]. The characteristics of bird eggshells depend on the effects of nesting environments and the bird nature on the pore number, the pore area, and the pore length. Some birds incubate their eggs in subterranean burrows which are characterized by high humidity and lower oxygen and higher carbon dioxide concentrations than normal. Birds nesting in these environments have eggshells with a porosity which is higher than expected from their egg weight. This greater porosity would not only help normalize water loss during incubation but would also lead to an easier exchange of respiratory gases [3-4]. Eggshells are a source of calcium that has a relatively lower density compared to mineral calcium carbonate and commercial calcium carbonate [5]. Thus eggshells are a good candidate material for a bulk quantity, inexpensive, lightweight and low load-bearing composite applications such as in the automotive industry, trucks, homes, offices, and factories [5] including as a filler in feed, fertilizer, paper, printing ink, pharmaceutical and cosmetic industries, and as starting materials for dielectrics such as $CaSiO_3$, $CaTiO_3$, $CaAl_2O_4$, gypsum ($CaSO_4$), and bio-catalysts [6-11].

Eggshell waste primarily contains calcium, magnesium carbonate (lime) and protein [12]. About 95 wt % of

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the dry eggshell is calcium carbonate weighing 5.5 g. The average eggshell contains about 0.3 wt % phosphorus, 0.3 wt % magnesium, and traces of sodium, potassium, zinc, manganese, iron and copper [13]. If the calcium from the shell is removed, the organic matrix material is left behind. This organic material has calcium binding properties, and its organization during the shell formation influences the strength of the shell. The organic material must be deposited so that the size and the organization of the crystalline components (mostly calcium carbonate) are ideal, thus leading to a strong shell. The majority of the true shell is composed of long columns of calcium carbonate. There are other zones that are involved in the self-organization giving the eggshell its strength properties. Thus, the shell thickness is the main factor, but not the only factor, that determines its strength. An eggshell that is smooth is desirable, as rough-shelled eggs tend to fracture more easily. Large eggs will usually break more easily than small ones. The shell-to-organic membrane relationship is also critical to good shell quality [13-14].

In this investigation, we studied the transformation, the composition, and the formation of phases by XRD and the N_2 adsorption-desorption isotherm by AUTOSORB of bird eggshells from calcium carbonate to calcium oxide by the calcination from room temperature to 900 °C for 1 h, 3 h, and 5 h at each temperature. Detailed investigations of the microstructures, the chemical composition, the functional groups, the particle size distribution, the density, the specific surface area, the average pore diameter, and the total pore volume are reported here.

Experimental

Materials

Raw bird eggshells were collected from a cafeteria. The raw bird eggshells were washed with tap water to remove the egg white and allowed to dry at room temperature. The raw bird eggshells were broken into small pieces, crushed by a porcelain mortar into fine particles, and then kept in desiccators at room temperature.

Instruments

A laboratory muffle furnace (Linn High Thermo GmbH, LM 412.27, model DC021032 with a thermocouple of type K, NiCr-Ni) was used to calcine samples from 27 °C to 900 °C in order to determine the physical properties such as color, softness, and odor. The raw bird eggshells were put in an alumina crucible in the muffle furnace and calcined at 300 °C, 500 °C, 700 °C, and 900 °C for 1 h, 3 h, and 5 h with a heating rate of 10 Kminute^{-1}.

Cumulative and fractional distributions were measured using a particle size analyzer (Mastersizer S long bed, model Polydisperse 2.19). The samples were dispersed in a water medium and vibrated in an ultrasonic cleaner for 20 minute.

Fourier transform infrared spectra (FTIR) were recorded on a spectrometer (Perkin Elmer, model Spectrum One) with a spectral resolution of 4 cm^{-1}. The samples were measured by mixing with single-crystal potassium bromide, KBr.

Chemical compositions were obtained using X-ray fluorescence (XRF) (Philips, model PW 2400) at a tube current of 1000 μA with an acquisition lifetime of 30 s. Data values were calculated following the theoretical formula and fundamental parameters.

X-ray diffraction (XRD) was taken and analyzed using an AXS analyzer (Bruker, D8 Discover) with a VANTEC-1 Detector. Samples were analyzed using a double-crystal wide-angle goniometry. Scans were measured from 10 ° to 80 ° 2θ at a scan speed of 5 ° 2θminute^{-1} in 0.05 ° or 0.03 ° 2θ increments using CuK_α radiation (λ = 0.15406 nm). Peak positions were consistent with those of the International Center for Diffraction Data Standard (JCPDS) patterns to identify crystalline phases.

Micrographs were obtained using a transmission electron microscope (TEM, JEM-2100) equipped with EDS for X-ray microanalysis and NBD for nano-beam diffraction. The TEM sample preparation of the raw bird eggshells and calcined bird eggshells was carried out on a grid to investigate the morphology and the microstructure. The acceleration voltage was between 80 kV to 200 kV with the magnifications between 50 and 1.5 million times.

The thermal properties were measured using a differential scanning calorimeter (DSC, NETZSCH 409) and a simultaneous thermal analyzer (STA, NETZSCH 409). The samples were tested with a heating rate 10 Kminute^{-1} under an air atmosphere.

True density of samples was measured by a gas pycnometer (Quantachrome, Ultra pycnometer 1000).

The specific surface area, the adsorption and/or desorption isotherms, the pore size and the surface distributions were measured using an AUTOSORB-1 (QUANTACHROME) by determining the quantity of gas adsorbed onto or desorbed from the solid surface at some equilibrium vapor pressure by the static volumetric method. The AUTOSORB-1 has the capability of measuring adsorbed or desorbed volumes of nitrogen at relative pressures in the range 0.001 to slightly below 1.0. When krypton and the micro-pore options are added, the lower limit is extended to 1×10^{-6} and data points can be obtained at 1×10^{-7}. This volume-pressure data can be reduced by the AUTOSORB-1 software into the BET (Brunauer-Emmet-Teller) surface area (single and/or multipoint), the Langmuir surface area, the adsorption and/or desorption isotherms, the pore size and surface area distributions, the micro-pore volume, and the surface area using an extensive set of built-in data reduction procedures. The determination of the surface area of solid materials involves the use of the BET equation as follows:

$$\frac{1}{W((P_0/P)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \quad (1)$$

where W is the weight of gas adsorbed at a relative pressure, P/P_o, W_m is the weight of adsorbate constituting a monolayer of surface coverage; and C is constant related to the energy of adsorption in the first adsorbed layer and consequently its value is thus an indication of the magnitude of the adsorbent/adsorbate interactions.

The specific surface area, S, of the solid can be calculated from the total surface area and the sample weight, according to equations 2 and 3 as follows:

$$S = S_t / W \tag{2}$$

$$S = \frac{W_m N A_{cs}}{M} \tag{3}$$

where S is the specific surface area of the solid, S_t is the total surface area, W is the sample weight, N is Avogadro's number (6.023×10^{23} molecules/mol), M is the molecular weight of the adsorbate, and A_{cs} is the area occupied by one adsorbate molecule (16.2×10^{-20}m^2 for N_2 and 19.5×10^{-2} m^2 for Kr). There are three types of porosity classifications by gas adsorption: (i) pores with openings exceeding 500 Å in diameter (called "macro-pores"); (ii) "micro-pores", which describes pores with diameters not exceeding 20 Å; and (iii) pores of intermediate size (called "meso-pores"). The adsorption isotherm is obtained point-by-point on the AUTOSORB by admitting to the adsorbent successive known volumes of nitrogen and then measuring the equilibrium pressure. Similarly, a desorption isotherm can be obtained by measuring the quantity of the gas removed from the sample as the relative pressure is lowered. All adsorption isotherms may be grouped into one of the six types as shown in Fig. 1.

Types IV and V, associated with meso-porosity, usually exhibit a hysteresis between the adsorption and desorption isotherms. The types of hysteresis loops explain the pore characteristics, i.e. cylindrical, slit-shaped, ink-bottle, and wedge-shaped pores with narrow necks at one or both open ends [15]. Characteristically, the hysteresis loops in all isotherms close before reaching a relative pressure of 0.3 in the desorption process, except when micro-porosity is present.

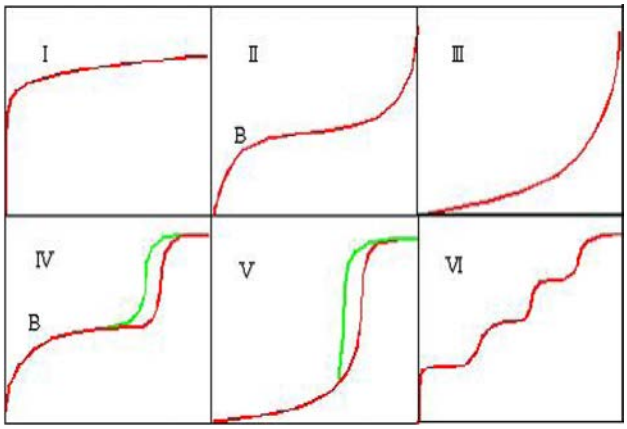

Fig. 1. Types of Isotherm.

Pyrolysis of eggshells

Approximately 1.00 g of cleaned and crushed with a porcelain mortar of raw bird eggshells were put in an alumina crucible and pyrolyzed in the muffle furnace under an air atmosphere at various temperatures from room temperature up to 900 °C, for 1 h, 3 h, and 5 h at each temperature with a heating rate 10 Kminute^{-1}. The reaction was completed after the pyrolysis, Eq. (4). The samples were allowed to cool down within 10 minutes to 20 minutes after bringing out from the muffle furnace and kept away from moisture to prevent the hydrolysis of Eq. (5). The raw bird eggshells and the pyrolyzed samples were subsequently characterized by STA, XRD, FTIR, TEM, BET, and the particle size analyzer.

$$CaCO_3 \xrightarrow{\text{Pyrolysis}} CaO + CO_2 \tag{4}$$

$$CaO + H_2O \xrightarrow{\text{Hydrolysis}} Ca^{2+} + 2OH^- \tag{5}$$

Results and Discussion

Physical caracterizations of raw and calcined bird eggshells via pyrolsis

Data of the specific surface area, the total pore volume, the average pore diameter, and the true density values between raw bird eggshells and calcined bird eggshells at 900 °C for 1 h are shown in Table 1. The specific surface area, the total pore volume, the average pore diameter, and the true density of the raw bird eggshells are 0.68 m^2/g, 4.60×10^{-3} cm^3/g, 267.90 Å, and 1.91 g/cm^3, respectively. The specific surface area, the total pore volume, the average pore , and the true density of the calcined bird eggshells at 900 °C for 1 h are equal to 7.20×10^{-3} cm^3/g, 82.99 Å, and 2.88 g/cm^3, respectively. The pyrolysis of raw bird eggshells at 900 °C for 1 h apparaently increases the specific surface area, the total pore volume, and the true density, whereas the average pore diameter of calcined particles decreases. The powder obtained after the calcination at 900 °C for 1 h is fine, soft, of a white color, odorless, and dense. The particle size distributions of the raw bird eggshells and the calcined bird eggshells at 900 °C for 1 h are shown in Figs. 2a and 2b, respectively. The particle sizes (d_{10}, d_{50}, and d_{90}) of the raw bird

Table 1. Specific surface area and density of raw bird eggshells and calcined bird eggshells at 900 °C for 1 h.

Samples	Multiple point BET (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (Å)	True density (g/cm^3)
Raw bird eggshells	0.68	4.60×10^{-3}	267.9	1.91
Bird eggshells 900_1	3.47	7.20×10^{-3}	82.9	2.88

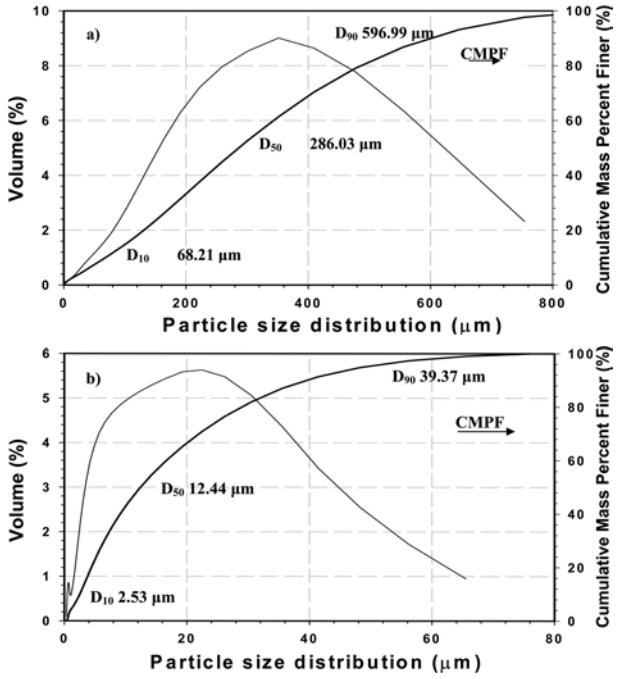

Fig. 2. a) Particle size distribution and cumulative mass percentage of raw bird eggshells. b) Particle size distribution and cumulative mass percentage of calcined bird eggshells at 900 °C for 1 h.

Table 2. Comparison of the true density of samples measured by a gas pycnometer.

Samples	True density (g/cm^3)
Raw bird eggshells	1.91
Raw duck eggshells	2.25
Raw chicken eggshells	2.20
Bird eggshells calcined 900_1	2.88
Duck eggshells calcined 900_1	2.84
Chicken eggshells calcined 900_1	2.16

(Quantachrome, Ultrapycnometer 1000)

eggshells are 68.21 µm, 286.03 µm, and 596.99 µm, respectively; they are larger than the particle sizes of d_{10}, d_{50}, and d_{90} of the calcined bird eggshells which are equal to 2.53 µm, 12.44 µm, and 39.37 µm, respectively.

Table 2 shows true density values of the raw eggshells and the calcined eggshells at 900 °C for 1 h obtained from bird, duck, and chicken. The data indicate that the eggshells are slightly different due to species, size, shape, feed, environmental nature including incubation.

The chemical composition data of the raw bird eggshells are tabulated in Table 3. Most inorganic compounds in the raw bird eggshells are calcium carbonate (96.23 wt %) and other inorganic compounds: Na_2O; MgO; SiO_2; P_2O_5; K_2O; SrO, and organic matter including protein of 3.77 wt %.

Simultaneous thermal analysis (STA) was used to analyze the thermal reaction or the endothermic-

Table 3. Chemical compositions analysis of raw bird eggshells by XRF.

Compounds	Element (wt %)
Na_2O	0.23
MgO	1.12
SiO_2	0.04
P_2O_5	1.19
SO_3	0.98
Cl	0.06
K_2O	0.11
SrO	0.02
$CaCO_3$	96.23

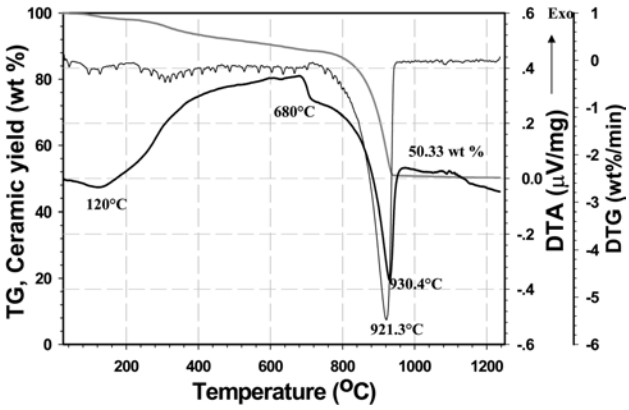

Fig. 3. Thermal analysis of raw bird eggshells from room temperature to 1200 °C with a heating rate 10 $Kminute^{-1}$ under air atmosphere by STA.

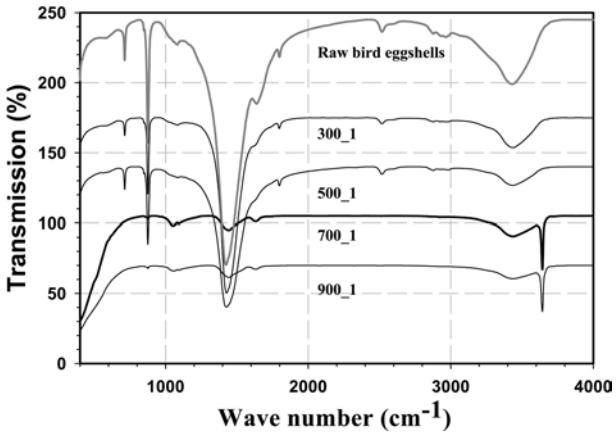

Fig. 4. FTIR spectra: raw bird eggshells and calcined bird eggshells at 300 °C, 500 °C, 700 °C, and 900 °C for 1 h.

exothermic reaction (DTA mode) and the percentage of ceramic yield (TGA mode) of the raw bird eggshells from room temperature to 1200 °C, as shown in Fig. 3. The DTA curve shows an onset at 861.5 °C. Three peak positions belonging the endothermic reaction of the raw bird eggshells occur at 120 °C, 680 °C, and 930 °C, respectively, can be identified as the decompositions of moisture H_2O, the volatile organic matter, and the emission of CO_2. The thermogravimetric TG/DTG plot indicates that the percentage of ceramic yield from

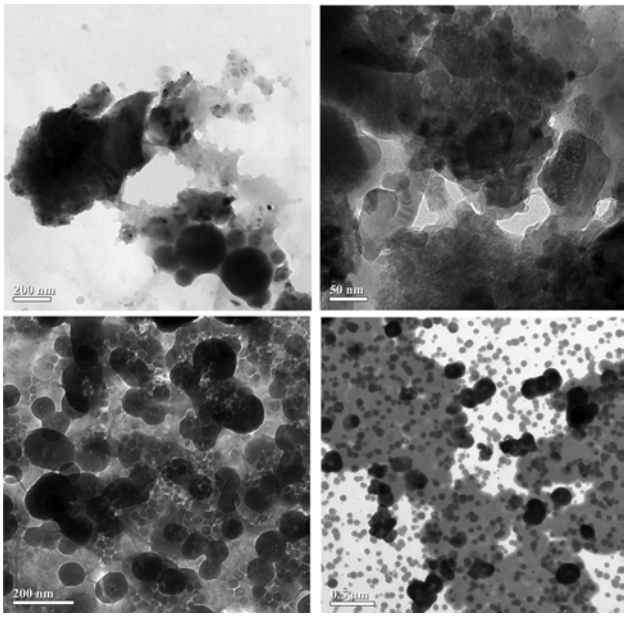

Fig. 5. Nanostructure of raw bird eggshells and calcined bird eggshells at 900 °C for 1 h: a) and b) raw bird eggshells; c) and d) calcined bird eggshells at 900 °C for 1h (900_1).

Table 4. Quantitative analysis of calcined bird eggshells from room temperature to 900 °C for 1 h, 3 h, and 5 h by X-ray diffraction.

Sample	$CaCO_3$ (Calcite) (Wt%)	CaO (Lime) (Wt%)	$Ca(OH)_2$ (Portlandite) (Wt%)	$CaCO_3$ (Aragonite) (Wt%)	MgO (Periclase) (Wt%)
Bird 900_5	-	97.20	1.05	0.09	1.65
Bird 900_3	-	97.23	1.29	0.09	1.39
Bird 900_1	-	97.41	1.13	0.07	1.40
Bird 700_5	70.14	28.78	1.06	0.01	-
Bird 700_3	87.07	12.44	0.48	0.01	-
Bird 700_1	99.39	0.61	-	-	-
Bird 500_5	~ 100	-	-	-	-
Bird 500_3	~ 100	-	-	-	-
Bird 500_1	~ 100	-	-	-	-
Bird 300_5	~ 100	-	-	-	-
Bird 300_3	~ 100	-	-	-	-
Bird 300_1	~ 100	-	-	-	-
Raw bird eggshells	~ 100	-	-	-	-

room temperature to 1200 °C of the raw bird eggshells to be 50.33 wt %, due to the carbon dioxide release in a single step.

FTIR spectra of the raw bird eggshells before and after the calcinations at 300 °C, 500 °C, 700 °C, and 900 °C are shown in Fig. 4. The characteristic peaks of the raw bird eggshells are consistent with the CAS [*471-34-1*] at the wavelength from 400 cm^{-1} to 4000 cm^{-1}. The bands at 875.08 cm^{-1} and 1423.55 cm^{-1}

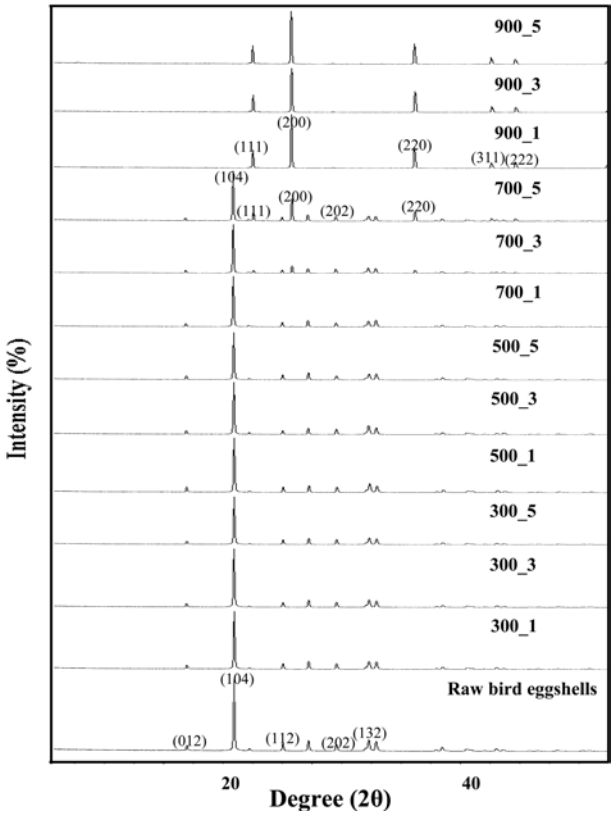

Fig. 6. XRD peak patterns and phase transformation of samples (raw bird eggshells and calcined bird eggshells) from 25 °C to 900 °C for 1 h, 3 h, and 5 h.

are associated with the vibrations of the carbonate groups. The raw bird eggshell and the calcined bird eggshell samples at 300 °C and 500 °C for 1 h possess the characteristic bands of the calcium carbonate structure at 713 cm^{-1}, 875 cm^{-1}, 1423 cm^{-1}, 1798 cm^{-1}, 2518 cm^{-1}, and 3435 cm^{-1}. The FTIR spectra of the calcined bird eggshells at 700 °C and 900 °C for 1 h indicate bands at 3643 cm^{-1} strong ν(O-H), 3435 cm^{-1} ν(O-H), 1630 cm^{-1} strong ν(C=O), and 500-580 cm^{-1} ν(Ca-O).

TEM images of the raw bird eggshells and the calcined bird eggshells at 900 °C for 1 h are shown in Fig. 5. The raw bird eggshell microstructures are shown in Figures 5a and 5b. The calcined bird eggshell microstructures are shown in Figures 5c and 5d. TEM images of the calcined bird eggshells indicate finer particles and smaller grain sizes than those in the TEM images of the raw bird eggshells, consistent with the particle size analysis.

Phase transformation of bird eggshells via pyrolysis by XRD

X-ray diffraction was used to study qualitatively and quantitatively the structures of the bird eggshells. X-ray diffraction spectra of samples were obtained with CuK_α radiation (λ = 0.15406 nm) in a scan range 5 ° to 80 ° (2θ). The quantitative analyses of the raw bird eggshells and the calcined bird eggshells are shown in Table 4. The

Table 5. Angle and plane positions of compounds as investigated by X-ray diffraction.

Compounds	Patterns	Degrees (2θ)	Planes (hkl)	Structures
$CaCO_3$ Calcium carbonate	01-085-1108	29.466	(104)	Rhombohedral R-3c
		43.244	(202)	
		47.625	(018)	
Calcium carbonate Aragonite	01-071-2392	37.365	(112)	Orthorhombic Pmcn
		47.553	(132)	
		56.851	(151)	
CaO Calcium oxide Lime	01-077-2376	37.377	(200)	Face-centered cubic Fm-3m
		53.892	(220)	
		67.420	(222)	
$Ca(OH)_2$ Calcium hydroxide Portlandite, Syn	01-087-0673	34.111	(101)	Hexagonal P-3m1
		62.649	(021)	
		64.258	(013)	
MgO Magnesium oxide, Periclase, Syn	01-077-2364	42.941	(200)	Face-centered cubic Fm-3m
		62.348	(220)	
		36.962	(111)	

phase transformation of the bird eggshells from room temperature to a high temperature of 900 °C is shown in Fig. 6 and the data are tabulated in Table 5. The raw bird eggshell peaks indicate approximately 100 wt % of calcium carbonate structures belonging to calcite ($CaCO_3$) rhombohedral; R-3c; JCPDS No. 01-085-1108, and a small amount of aragonite ($CaCO_3$) orthorhombic; Pmcn; JCPDS No. 01-071-2392. The calcinations of the bird eggshells at 300 °C and 500 °C for 1 h, 3 h, and 5 h do not induce the phase transformation. The phase transformation evidently occurs at 700 °C. A longer calcination time induces a higher degree of the phase transformation at 700 °C as shown by the data tabulated in Table 4, consistent with the XRD phase transformation shown in Fig. 6. When the bird eggshells are calcined at 900 °C for 1 h, 3 h, and 5 h, the data indicate complete phase transformation from calcium carbonate ($CaCO_3$) to calcium oxide (CaO) or lime; face-centered cubic; Fm-3m; JCPDS No. 01-077-2376, mixed with a small amount of calcium hydroxide ($Ca(OH)_2$) or portlandite; hexagonal; P-3 m1; JCPDS No. 01-087-0673 due to the moisture absorption, and magnesium oxide (MgO) or periclase; face-centered cubic; Fm-3m; JCPDS No. 01-077-2364. The magnesium compounds obtained in the bird eggshells are consistent with the results reported by Board *et al.* [16].

Moreover, the calcination of the bird eggshells at 900 °C for 1 h induces the complete phase transformation without the need of longer calcination times of 3 h or 5 h. The longer calcination time at 900 °C influences only on the moisture sensitivity to form calcium hydroxide ($Ca(OH)_2$). The main peaks of the bird eggshells before and after the calcination appear at $2\theta = 29.466$ ° and 37.377 °, respectively. In addition, several peaks of

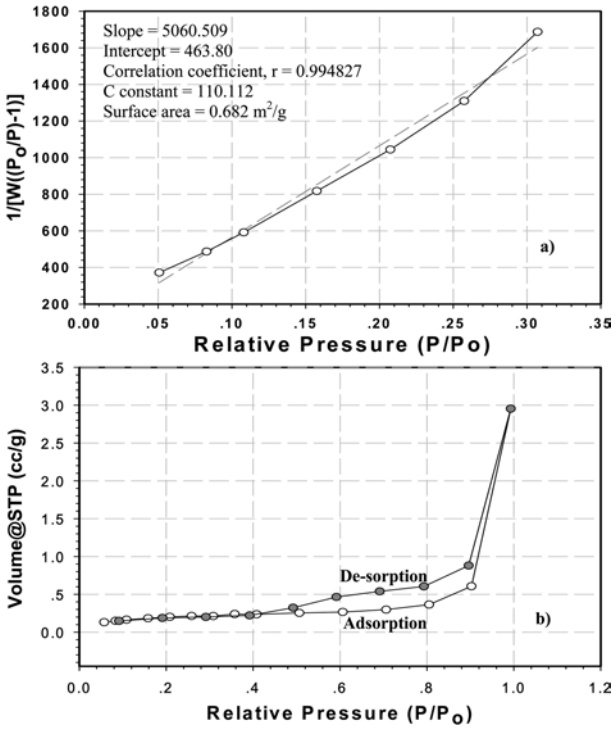

Fig. 7. a) Specific surface area of raw bird eggshells versus the relative pressure, as measured by the BET method. b) Adsorption-desorption isotherm of raw bird eggshells as measured by AUTOSORB-1.

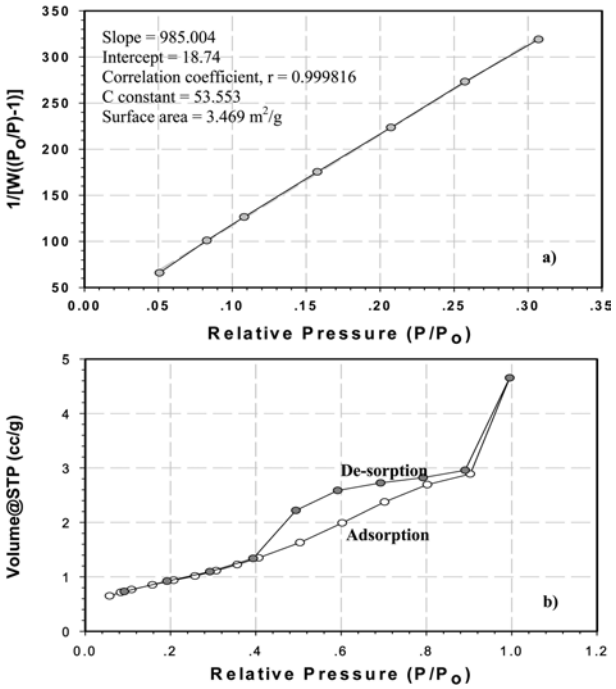

Fig. 8. a) Specific surface area of calcined bird eggshells at 900 °C for 1 h as measured by the BET method. b) Adsorption-desorption isotherm of calcined raw bird eggshells at 900 °C for 1 h as measured by AUTOSORB-1.

calcium oxide appear at $2\theta = 34.111$ °, 36.962 °, 53.892 °, 62.348 °, and 67.420 °.

Specific surface area and isotherm of bird eggshells via pyrolsis by BET

The specific surface area and the N_2 adsorption-desorption isotherm of the raw bird eggshells at a room temperature (27 °C) are shown in Figs. 7a and 7b, respectively. The specific surface area of the raw bird eggshells is 0.682 m^2/g, whereas the isotherm corresponds to the type IV hysteresis loop of the adsorption and the desorption reactions associated with the meso-porosity range. Figs 8a and 8b show the specific surface area and the N_2 adsorption-desorption isotherm of calcium oxide of the bird eggshells calcined at 900 °C for 1 h. The specific surface area, the total pore volume, and the average pore diameter of the bird eggshells calcined at 900 °C for 1 h are equal to 3.47 m^2/g, 0.0072 cm^3/g, and 82.99 Å, respectively. In addition to, the isotherm of the calcined eggshells at 900 °C for 1 h corresponds to the type IV hysteresis loop of the adsorption and the desorption reactions associated with the meso-porosity range. Calcium oxide is in the range of the meso-pore because the pore diameter is in the range of 20 Å-500 Å (2 nm-50 nm), following the Kelvin equation [15].

Conclusions

Raw bird eggshells were investigated for the crystal structure and the phase transformation qualitatively and quantitatively by X-ray diffraction analysis. The phase transformation of bird eggshells started whenever the calcination was above 700 °C and the phase transformation was complete at 900 °C for 1 h. 100 wt % calcite ($CaCO_3$) of the raw bird eggshells at room temperature transforms into 97.41 wt % lime (CaO) mixed with small amounts of calcium hydroxide ($Ca(OH_2)$) and magnesium oxide (MgO) via the pyrolysis at 900 °C for 1 h. The specific surface area, the total pore volume, and the average pore diameter of CaO were equal to 3.47 m^2/g, 0.0072 cm^3/g, and 82.99 Å, respectively. The adsorption and the desorption isotherms of the calcined eggshells at 900 °C for 1 h corresponds to the type IV hysteresis loop associated with the meso-pore range because the pore diameter lies between 20 Å-500 Å (2 nm-50 nm).

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