

Ceramic granules forming from calcium sodium aluminosilicate and carboxymethyl cellulose

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Calcium sodium aluminosilicate with a molar ratio of 1 : 1 : 2 : 8 of CaO : Al₂O₃ : Na₂O : SiO₂, was successfully synthesized, by a sol-gel process using chicken eggshell powder as the starting material, through the calcination at 300 °C for 1 hr. Carboxymethyl cellulose was used as an organic binder to produce the granulation of the ceramic powder without altering any ceramic powder properties. The calcium sodium aluminosilicate granules possess the specific surface area of 38.89 m² g⁻¹, the pore volume of 0.37 cm³, the average pore diameter of 38.34 nm, and the true density of 1.96 g cm⁻³. The obtained ceramic granule is of a very fine particle and it is white in color. The obtained ceramic granules possess good flowing ability and uniform granule size. Fourier transformation infrared spectra (FTIR), X-ray diffraction patterns (XRD), scanning electron micrographs (SEM), transmission electron micrographs (TEM), and physical properties are reported to confirm the existence of the ceramic granules.

Key words: Wet granulation, Ceramic-polymer composite, Carboxymethyl cellulose, Ceramic flow property, Calcination, Zeolite.

Introduction

The egg and egg derivative consumptions produce a great amount of residue shells which pose an environmental pollution through microbial actions. The Agricultural Statistics of Thailand reported the egg production of approximately 9.8×10^9 hens' eggs in 2011 and the number tends to increase indefinitely. The by-product eggshell represents approximately 11% w/w of the total weight (about 50-60 g) of a hen egg. Therefore, the hen eggshells yield approximately 60×10^6 metric tons of the by-product per year in Thailand alone. The eggshells such as from hen, duck, bird, goose, partridge bird are important sources for calcium carbonate, calcium oxide, and calcium hydroxide potentially used in various applications: filler in feed, fertilizer, paper, printing ink, pharmaceutical and cosmetic products, starting materials of dielectrics such as CaSiO₃, CaTiO₃, CaAl₂O₄, gypsum (CaSO₄), bio-catalysts for bio-diesel and bio-gasoline [1-10]. Most of eggshell by-products are commonly disposed of by land filling without any pretreatment. This causes odors from biodegradation, microbial actions, and a change in the quality of soil. Eggshells are generally composed of three layers: a thin cuticle outer layer, a thick palisade middle layer, and a thin mammillary inner layer. In particular, the thick palisade middle

layer has many large pores. Therefore, it is possible for the eggshell to enhance the catalytic activity per unit mass using the porous palisade layer with a higher fraction.

The porous-solid ceramic namely calcium sodium aluminosilicate with the mole ratio of 1 : 1 : 2 : 8 of CaO : Al₂O₃ : Na₂O : SiO₂, was previously obtained from eggshells via the sol-gel process through the calcination at 300 °C for 1 hr, as very fine powder [10-15]. Calcium sodium aluminosilicate is a kind of heterogeneous solid catalysts that is implemented in the environmental protection and in the waste treatment. However, fine particles having low dispersion may affect several operations in the powder processing; flow, storage, mixing, fluidization, moisture absorption, and pressing. There are several methods to solve the poor particle dispersion, in order to reduce packaging problem, to reduce chemical usage, to comply with air pollution regulation, and to decrease energy consumption. The dispersion can be controlled by modifying the characteristics of the particles or by changing the properties of a dispersed medium, at the same time avoiding any characteristics change of the powders. Small particles are modified for free flowing, poor cohesive forces, and with no caking problem. Two kinds of industrial processes mostly used are the wet granulation and the spray drying; they normally lead to spherical final products [16].

Granulation, also known as agglomeration, pelletisation or balling, is the process of agglomerating fine particles together into larger, semi-permanent aggregates (granules) in which the original particles can still be distinguished.

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It consists of a combination of three rate processes (wetting and nucleation, consolidation and growth, and attrition and breakage) [17]. The obtained granules can be used as an adsorbent or a catalyst because of high packing density with minimum air entrapment. On the other hand, a narrow size distribution is preferred in fixed bed reactors to reduce the pressure drop. Wet granulation is the process of bringing material together, by combining smaller particles into larger agglomerates and granules, with a binding agent to enhance flow property and dusting behavior [18]. In the wet granulation process, the capillary and viscous forces from the binder tend to agglomerate particles. The organic liquid binds the particles together until more permanent bonds are established, leading to the granule formation. Overall, the organic binder induces the appropriate cohesive strength and free flowing properties [17, 19-20].

Carboxymethyl cellulose (CMC) is microcrystalline organic colloidal particle; it is a non-toxic binder and the most important commercial cellulose functioning as an organic binder in the granulation process. Applications of CMC based on its rheological properties are: fillers, extenders, glues, hydrophilic colloid thickeners in detergents, oil drilling mud, and wall paper glues. High purity CMC grade is found in pharmaceuticals, toothpaste, and in medical and food industries [21-26].

The obtained calcium sodium aluminosilicate particles are of a fine powder and high specific surface area, therefore, it is potential to apply as catalyst and adsorbent. However, the flow ability problem of calcium sodium aluminosilicate is not suitable for using as column packed bed, storage, or compression. Therefore, the objective of this work is to fabricate ceramic granules of calcium sodium aluminosilicate, with improve flow properties for use, storage, and modified applications. This was carried out by mixing the ceramic powder with sodium carboxymethylcellulose (CMC) which acts as a binder, a lubricant, a stabilizer, a thickener, a gelling agent, and a wet tack with long lasting adhesion. The calcium sodium aluminosilicate ceramic granule detailed characteristics such as bulk density, microstructures, X-ray diffraction patterns (XRD), the particle size distribution, FTIR, the specific surface area, the isotherm plot, and the true density are investigated and reported here.

Experimental

Materials and methods

Calcium oxide (CaO) was prepared from the pyrolysis of chicken eggshells collected from a cafeteria at Kasetsart University, Bangkok, Thailand. Hydrophilic fumed silica (SiO_2 , 99.8% pure, the specific surface areas of $206 \text{ m}^2 \text{ g}^{-1}$, the pH value of

3.9, and the average particle size of 40 microns) was obtained from WACKER Chemie AG, Germany. Precipitated sodium aluminosilicate (82% silica, 10% alumina, 6% sodium oxide, and 0.04% iron oxide), was obtained from United Silica (Siam) Ltd., Thailand. Sodium hydroxide pellets (98% pure) were obtained from Molecule Co., Ltd., Thailand. Hydrochloric acid (Analytical Reagent grade, AR) was purchased from Lab-Scan Co. Ltd., Thailand. Carboxymethyl cellulose (CMC 10000) or a cellulose gum powder, as supplied by Amarin Ceramics Corp., Ltd., Thailand, was used as the binder in the granule preparation. CMC 10000 is highly purified sodium carboxymethyl cellulose. The sodium content (dry basis), the moisture content, the degree of substitution, the pH value, and the viscosity (Brookfield LVF 60 rpm) of CMC 10000 are 99.5% min, 8%, 0.60-0.95, 6-8, 700-1500 mPas (25 °C, 1%), respectively.

Instruments

A laboratory muffle furnace (Linn High Thermo GmbH, LM 412.27, model DC021032 with the thermocouple of type K, NiCr-Ni) was used to prepare the CaO samples from eggshells. The calcination was carried out in an alumina crucible under the heating rate of $10 \text{ }^\circ\text{C/min}$.

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 min. Cumulative and fractional distributions were measured by using a particle size analyzer (Mastersizer S, Model Polydisperse 2.19).

Fourier transform infrared spectra (FTIR) were recorded (PerkinElmer, model Spectrum One spectrometer) with a spectral resolution of 4 cm^{-1} using transparent KBr pellets obtained by mixing 0.001 g of a sample with 0.06 g of KBr and hydraulically pressed.

X-ray diffraction patterns (XRD) were analyzed using an X-ray diffractometer (Bruker AXS analyzer (D8 Discover) with a VANTEC-1 Detector) consisting of $\text{CuK}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The double-crystal wide-angle goniometry was used to analyze the samples. Scanning was operated from 5° to $80^\circ 2\theta$ at a scan speed of $5^\circ 2\theta \text{ min}^{-1}$ in 0.05° or 0.03° .

Micrographs were obtained using a transmission electron microscope (TEM, JEM-2100) equipped with EDX for the X-ray microanalysis and for the nano beam diffraction (NBD). Ceramic granule samples were cut to obtain a thin foil for the beam to penetrate to investigate the morphology and microstructure.

Scanning electron (SEM) micrographs were obtained from a scanning electron microscope (JEOL, Model 5200). The ceramic granules were immobilized on stubs using a carbon paste and were sputter-coated to $\sim 0.1 \text{ }\mu\text{m}$ with gold to improve electrical conductivity and quality of the SEM images.

True density of the samples was measured by a gas pycnometer (Quantachrome, Ultra pycnometer 1000). Bulk density of granules was measured on the basis of its mass (m) and volume (V) according to ASTM E727/E727M-08 in equation (1);

$$\rho_b = \frac{m}{V} \quad (1)$$

where ρ_b is the bulk density of granulation (g cm^{-3}), m is the mass (g), and V is the volume (cm^3).

The specific surface area, the adsorption and/or desorption isotherms, the pore size and the surface distributions were measured using an AUTOSORB-1 (Quantachrome) based on the BET (Brunauer-Emmet-Teller) equation:

$$\frac{1}{W((P_o/P)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_o} \right) \quad (2)$$

where W is the weight of gas adsorbed at a relative pressure, P/P_o , W_m is the weight of adsorbate constituting of a monolayer of surface coverage; and C is the 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):

$$S = S_t/W \quad (3)$$

$$S_t = \frac{W_m N A_{cs}}{M} \quad (4)$$

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^{-1}), 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^{-20} m^2 for Kr). There are three types of porosity classifications by gas adsorption: (i) pores with openings exceeding 500 Å in diameter are called "macropores"; (ii) "micropores", which can be identified with pores of diameters less than 20 Å; and (iii) pores of intermediate sizes between the above pores are called "mesopores".

Calcium sodium aluminosilicate ceramic powder preparation by sol-gel process [15]

Calcium chloride solution preparation: calcium oxide (CaO) was prepared from eggshells by the pyrolysis. The eggshells were cleaned and crushed in an alumina crucible, calcined with the muffle furnace under an air atmosphere at 900 °C, for 1 hr at a 10 °C min^{-1} of heating rate, and then cooled in air. Calcium oxide (0.5 g) was dissolved in 20 ml of 1M HCl to obtain a solution.

Mixture of sodium aluminosilicate solution preparation: The mixture was obtained by mixing fumed silica (SiO_2) powder 0 to 0.5 g, precipitated sodium aluminosilicate, and 1.0 g of sodium hydroxide (NaOH) with 20 ml of distilled water.

Calcium sodium aluminosilicate preparation: The mixture solution of 2.3.1 and the mixture solution of 2.3.2 were mixed, and the solution of the mixtures changed into a gel within 5 hrs. The samples were allowed to age to obtain the particle growth for a duration of 24 hrs at room temperature. The molar ratios of the $\text{CaO} : \text{Al}_2\text{O}_3 : \text{Na}_2\text{O} : \text{SiO}_2$ were 1 : 1 : 2 : 8 by the sol-gel process at room temperature (25 °C). The gel samples were dried at 110 °C for 24 hrs and then calcined at 300 °C for 1 hr. All dried white powder samples were obtained.

Calcium sodium aluminosilicate ceramic granules preparation and classification

Calcium sodium aluminosilicate ceramic powder granules were produced directly from fine ceramic powders (10 g) premixed with a small percentage (0.20 g) of carboxymethyl cellulose (CMC) in 10 ml warm water (approximately temperature 60-70 °C) as a binder solution at room temperature. The mixture of calcium sodium aluminosilicate ceramic powder and the CMC binder solution was stirred for approximately 5 to 10 min. After few minutes, an agglomeration called a granule or seed formed initially. The growth of ceramic granules occurred by layering and by the

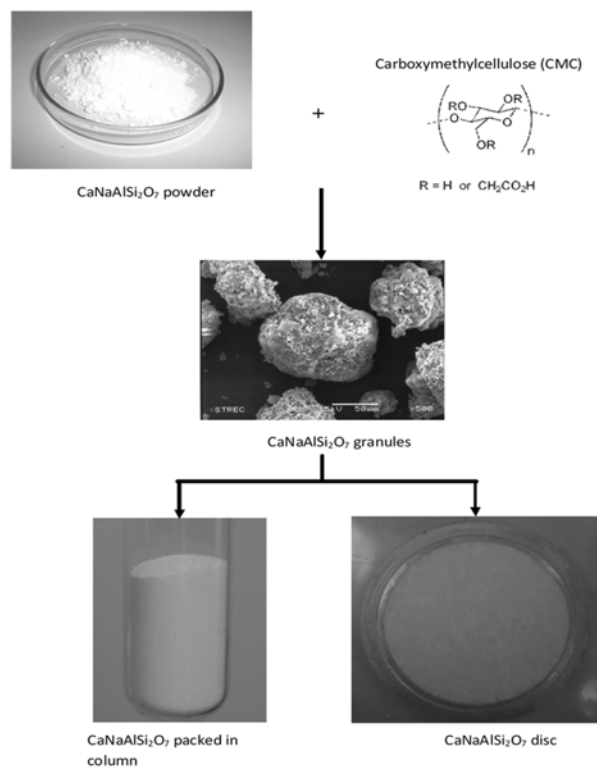


Fig. 1. Flowchart of calcium sodium aluminosilicate ceramic granules and disc formation.

agglomeration of particles. The growth of granules depends on the ratio between CMC and water (solution viscosity), temperature, and the effective adsorption of liquid into the agglomerate. The ceramic granules were put on the top tray and the stack of sieves was vibrated circularly by hand for 30 min. Granules were classified by the gravitation force during the sieving for 30 min. The obtained ceramic granule sizes were classified by passing them through the U.S. Standard sieves of the International Standards Organization (ISO). The sieves were arranged in a stack from the coarsest to the finest (65 mesh (212 μm), 100 mesh (150 μm), 150 mesh (106 μm), and 200 mesh (75 μm), respectively. The percentage of ceramic granules remaining was calculated for each sieve size. The obtained granules are with good flow ability, and of round shapes. The obtained ceramic granules can be packed into a column or pressed under pressure to measure the bulk density and to form ceramic discs, as shown in Fig. 1.

Results and Discussion

Characterizations of raw materials for porous-solid ceramic powder

Calcium oxide (CaO) was prepared from the pyrolysis of chicken eggshells. Raw eggshells were cleaned with tap water and dried at a room temperature. Then they were crushed by a porcelain mortar and kept in a desiccator until further use. The calcium oxide was successfully extracted by the pyrolysis technique at 900 °C for 1 hr, which produced the yield with a very high purity of 98.15%. The FTIR spectra 900_1 exhibit strong $\nu(\text{O-H})$ and $\nu(\text{Ca-O})$ vibrations. The broad peaks indicate the O-H stretching vibration $\nu(\text{O-H})$ of the calcium oxide (CaO), fumed silica (SiO_2), and aluminosilicate at 3,643 and 3,443 cm^{-1} , 3434 cm^{-1} , and 3435 cm^{-1} , respectively. They can be assigned to the water absorbed on the surface of the products. The band at 1630-1633 cm^{-1} can be attributed the O-H bending $\delta(\text{O-H})$ of CaO, SiO_2 and aluminosilicate. The characteristic peaks of the amorphous SiO_2 , CaO, and aluminosilicate correspond to $\nu(\text{Si-O-Si})$, $\nu(\text{Ca-O})$, and $\nu(\text{Al-O-Si})$ at 1108 and 810 cm^{-1} , 874 cm^{-1} , and 1079 and 791 cm^{-1} , respectively.

A phase transformation was investigated by XRD

patterns which reveal that the rhombohedral form of the calcium carbonate (calcite, CaCO_3), the main composition of eggshell, transforms into the hexagonal form of calcium oxide and hydroxide. The ceramic yield of calcium oxide content is equal to 74.42%, as characterized by STA [15]. The data suggests that calcium carbonate (CaCO_3) was converted to calcium oxide (CaO) with high purification. Both fumed silica (SiO_2) and aluminosilicate show amorphous phases in the XRD patterns. Therefore, all raw materials (CaO, SiO_2 , and aluminosilicate) for the ceramic compound preparation are of high purity suitable to prepare a porous-solid ceramic powder.

The specific surface area, the total pore volume, the average pore diameter, and true density of calcium oxide (CaO) values are 7.79 $\text{m}^2 \text{g}^{-1}$, 0.0072 $\text{cm}^3 \text{g}^{-1}$, 17.00 Å, and 2.16 g cm^{-3} , respectively. The specific surface area, the percentage of loss on drying, the pH value, the bulk density, true density, and the particle size of sodium aluminosilicate are 75 $\text{m}^2 \text{g}^{-1}$, 5.2, 10.0, 200 kg m^{-3} , 2.04 g cm^{-3} , and 45 microns, respectively [15].

Characterizations of calcium sodium aluminosilicate ceramic granules

The physical properties data of CaO, fumed silica, aluminosilicate, and calcium sodium aluminosilicate ceramic granules are tabulated in Table 1. The specific surface areas of CaO made from eggshells, fumed silica (SiO_2), aluminosilicate, and the calcium sodium aluminosilicate granules are 7.79, 206, 75, and 38.89 $\text{m}^2 \text{g}^{-1}$, respectively. The specific surface area of the calcium sodium aluminosilicate ceramic granules suggests it is in the range of mesoporous particles. True densities of CaO made from eggshells, fumed silica (SiO_2), aluminosilicate, and the calcium sodium aluminosilicate ceramic granule are 2.16, 2.12, 2.04, and 1.96 g cm^{-3} , respectively. The average pore diameter of the calcium sodium aluminosilicate ceramic granules is equal to 38.34 nm.

The particle size distribution of the ceramic powder is shown in Fig. 2. The d_{10} , d_{50} , d_{90} , and d_{avg} of the calcium sodium aluminosilicate ceramic powder are 2.67, 9.88, 29.10, and 13.27 μm , respectively.

FTIR spectra of the CaO made from eggshells, fumed silica, aluminosilicate, and the calcium sodium

Table 1. Physical properties of CaO, fumed silica, aluminosilicate, and calcium sodium aluminosilicate ceramic granules.

Samples	Specific surface area BET (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (Å)	True density (g/cm^3)
CaO	7.79	0.0072	17.00	2.16
Fumed silica (SiO_2)	206.00	—	—	2.12
Aluminosilicate	75.00	—	—	2.04
Calcium sodium aluminosilicate granules	38.89	0.3728	383.40	1.96

“—” means not measured.

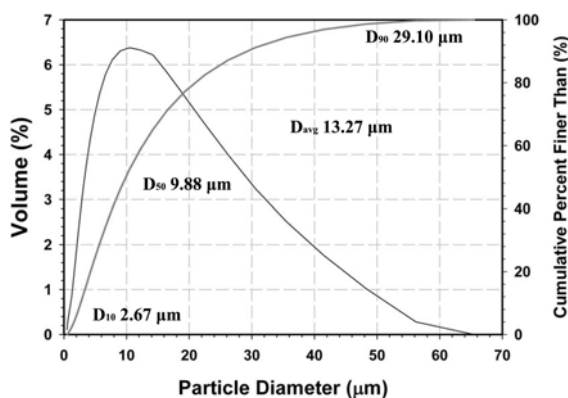


Fig. 2. Particle size distribution of calcium sodium aluminosilicate ceramic powder.

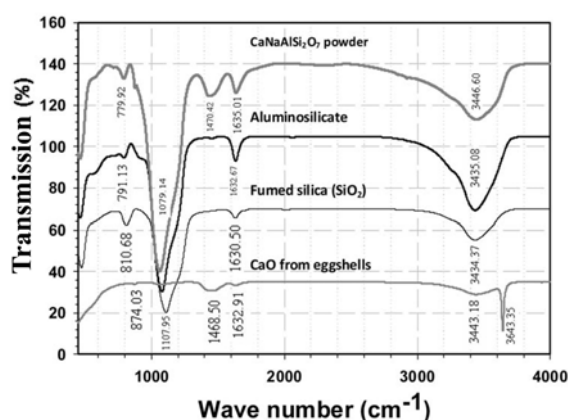


Fig. 3. FTIR spectra of CaO, fumed silica (SiO_2), aluminosilicate, and calcium sodium aluminosilicate ceramic powder.

aluminosilicate powder are shown in Fig. 3. The FTIR spectrum of the calcium oxide (CaO) exhibits peaks at 3600 cm^{-1} due to strong (O-H), 3450 cm^{-1} due to $\nu(\text{O-H})$, $2800\text{--}2970\text{ cm}^{-1}$ due to $\delta(\text{C-H})$, 1750 cm^{-1} of $\nu(\text{C=O})$, 1650 cm^{-1} due to strong $\nu(\text{C=O})$, and $500\text{--}580\text{ cm}^{-1}$ due to $\nu(\text{Ca-O})$. The FTIR spectra of the aluminosilicate and the fumed silica show a broad peak at 3450 cm^{-1} due to strong $\nu(\text{O-H})$, and at 540 cm^{-1} due to $\nu(\text{Al-O-C})$, $\nu(\text{Si-O-Al})$, $\nu(\text{Si-O})$, and $\nu(\text{Si-O-Si})$. The FTIR spectra of the calcium sodium aluminosilicate powder differ from the FTIR spectra of the raw materials (CaO, SiO_2 , and aluminosilicate); the peaks are at 1470 cm^{-1} due to strong $\nu(\text{C=O})$, $640\text{--}580\text{ cm}^{-1}$ due to $\nu(\text{Al-O})$, and nearly $500\text{--}550\text{ cm}^{-1}$ due to $\nu(\text{Al-O-C})$, $\nu(\text{Si-O-Al})$, $\nu(\text{Si-O})$, and $\nu(\text{Si-O-Si})$.

FTIR spectra of the calcium sodium aluminosilicate ceramic powder, CMC as the binder, and the calcium sodium aluminosilicate ceramic granules in the range of 4000 to 400 cm^{-1} are shown in Fig. 4. The FTIR spectrum of the calcium sodium aluminosilicate ceramic granules and CMC show peaks at 3433 cm^{-1} due to strong $\nu(\text{O-H})$ and 3436 cm^{-1} due to $\nu(\text{O-H})$, corresponding to the hydroxyl group of anhydroglucose units of cellulose molecule. Furthermore, the FTIR spectra of the calcium sodium aluminosilicate ceramic

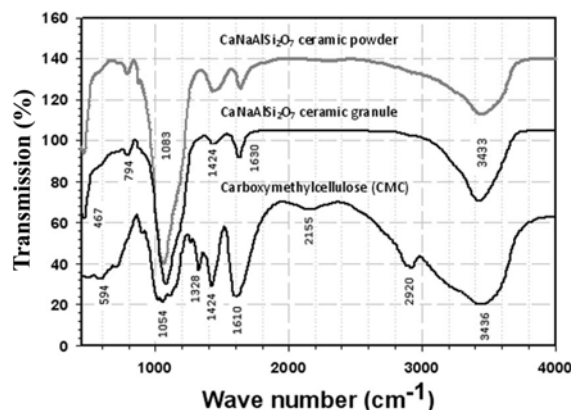


Fig. 4. FTIR spectra of carboxymethyl cellulose, calcium sodium aluminosilicate powder, and calcium sodium aluminosilicate ceramic granules.

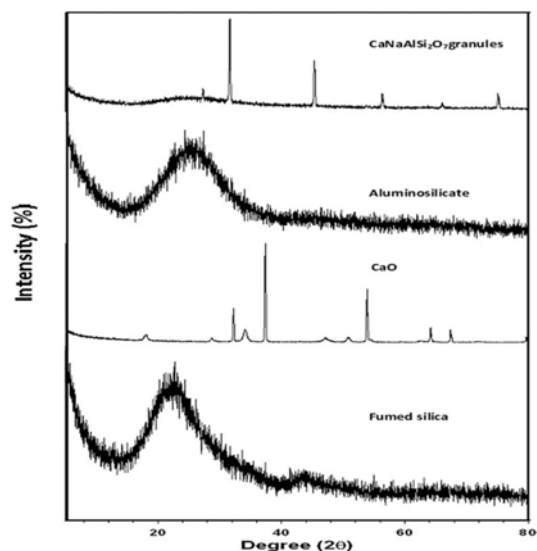
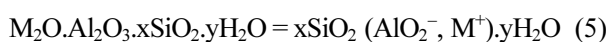


Fig. 5. XRD patterns of CaO, fumed silica (SiO_2), aluminosilicate, and calcium sodium aluminosilicate ceramic granules.

granules and carboxymethyl cellulose show peaks at 2920 cm^{-1} due to $\delta(\text{C-H})$ of CH_2 , 1610 cm^{-1} due to $\nu(\text{C=O})$ of the ketone group, 1424 cm^{-1} and 1328 cm^{-1} due to $\delta(\text{C-H})$ of CH_2 , 1054 cm^{-1} and 1083 cm^{-1} due to $\nu(\text{CH}_2\text{-OH})$ and $\nu(\text{C-O})$, and 594 cm^{-1} due to $\delta(\text{C-H})$.

XRD patterns of the fumed silica (SiO_2), CaO made from eggshells, the aluminosilicate, and the calcium sodium aluminosilicate ceramic granules are shown in Fig. 5. The XRD patterns of the fumed silica and the aluminosilicate exhibit an amorphous phase formation. The XRD pattern of the CaO made from eggshells shows a crystalline phase formation, corresponding to those assigned at the International Center for Diffraction Data (JCPDS) patterns, with numbers 85-1108 and 72-1651. With the peaks 2θ equal to 29.466 , 36.039 , 39.489 , 47.625 , and 48.615 , they correspond to the rhombohedral form of calcium carbonate (calcite, CaCO_3). The X-ray characteristic peaks and patterns of the calcium sodium aluminosilicate ceramic granules are

consistent with JCPDS numbers 71-2066, 77-2064, and 76-479. With the peaks at 2θ and (hkl) equal to 31.605 (211), 45.432 (220), 56.452 (222), 29.310 (201), 68.714 (521), and 75.263 (420), they correspond to the tetragonal form of calcium sodium aluminosilicate. The crystal structure of the calcium sodium aluminosilicate granule corresponds to the crystal structure shown in Fig. 5. The crystal structure of calcium sodium aluminosilicate suggests it is possible to express ion exchange in the general formula of sodium aluminosilicate. Ca^{2+} can be substituted for Na^+ at the site of monovalent. Furthermore, calcium sodium aluminosilicate is one kind of catalyst structures that are ion exchangers whose cations are catalytically active as shown in the equation (5).



Specific surface area and isotherm of calcium sodium aluminosilicate ceramic granules

The specific surface area and the N_2 adsorption-desorption isotherms of CaO from eggshells and the as-synthesized calcium sodium aluminosilicate granule, are shown in Fig. 6a and 6b. The specific surface area, the total pore volume, and the average porosity diameter of calcium sodium aluminosilicate granules are $38.89 \text{ m}^2 \text{ g}^{-1}$, 0.3728, and 38.34 nm, respectively. The pore size distribution vs. pore diameter of the calcium sodium aluminosilicate shows the pore diameter in the range of 20 Å to 500 Å, which can be called a mesoporous structure through its hysteresis loop, following the Kelvin equation. It is widely accepted that the desorption isotherm is more appropriate than the adsorption isotherm for investigating the pore size distribution of an adsorbent. The desorption branch of the isotherm, for the same volume of gas, shows a lower relative pressure, causing a lower free energy state. Thus, the desorption isotherm is close to the thermodynamic equilibrium. The high specific surface area and porosity of solid-porous particles are the most important properties required for removing pollutants, reagents separation, and products purification,

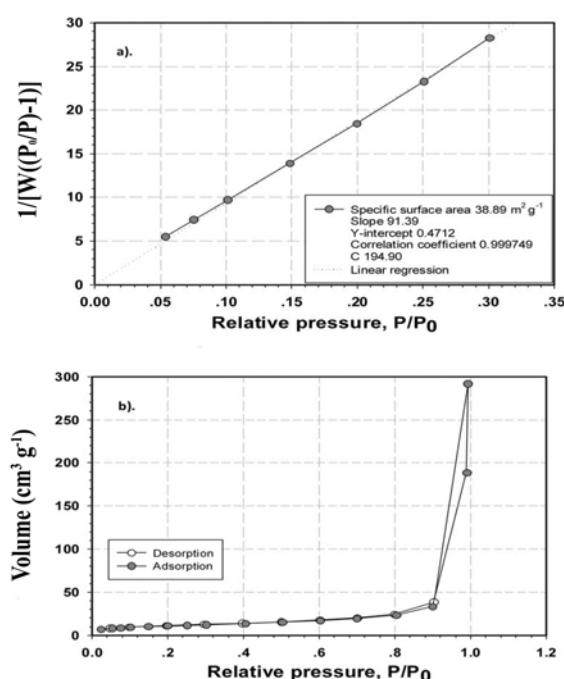


Fig. 6. (a) Specific surface area of calcium sodium aluminosilicate ceramic granules versus the relative pressure and (b) Isotherm plot of adsorption and desorption of calcium sodium aluminosilicate ceramic granules versus the relative pressure.

by acting as a heterogeneous catalysis; however its catalytic activity should be verified further. Calcium sodium aluminosilicate is one kind of porous-solid types whose pores arise from the intrinsic crystalline structure containing Al, Si, Ca, Na, and O. Al-O, and Si-O tetrahedral units cannot occupy the space perfectly, and therefore they produce cavities which are suitable for pollutant trapping or ion exchange.

Bulk density and micrographs of ceramic granules

Bulk density values of the calcium sodium aluminosilicate granules are data tabulated in Table 2. The bulk density values of the calcium sodium aluminosilicate ceramic granules of sizes 75, 106, 150, and 212 μm are 0.0329 ± 0.0124 , 0.0369 ± 0.0263 , 0.0381 ± 0.0304 , $0.0415 \pm 0.0258 \text{ g cm}^{-3}$, respectively.

Table 2. Bulk density of calcium sodium aluminosilicate ceramic granules.

Sieve size ^{a*} (mesh)	Average diameter of granules (μm)	Bulk density granules with pores (g/cm^3)	Amount granules with pores ^{b*} (%)
200	75	0.0329 ± 0.0124	72.61
150	106	0.0369 ± 0.0263	12.74
100	150	0.0381 ± 0.0304	8.28
65	212	0.0415 ± 0.0258	6.36

^{a*} U.S.A Standard Sieve Series-ASTM Specification E11-70.

^{b*} mean amount granules with pores in unit of percent when granules classified by standard screens arranged in a stack from the coarsest to the finest (65, 100, 150, 200, and solid tray, respectively) with a pan below the bottom sieve to collect the fines. The calcium sodium aluminosilicate ceramic granules are introduced on the top screen and the stack of sieves is vibrated such that the ceramic granules will stratify by particle size through the sieves.

The percentages of granules or agglomeration on each sieve size were classified by passing them through the standard screens arranged in a stack from the coarsest to the finest 65 mesh (212 μm), 100 mesh (150 μm), 150 μm mesh (106 μm), and 200 mesh (75 μm), respectively, are 6.36%, 8.28%, 12.74%, and 72.61%, respectively. Aulton and Banks (1979) reported that as the wettability of the powder mixture increased, the mean granule size decreased [20]. Wetting and spreading can also be described using surface free energies. The spreading coefficient (λ) is a measure of the tendency of a liquid and a solid to spread over each other and is related to the works of adhesion and cohesion [17]:

$$\text{Work of cohesion for a solid: } W_{CS} = 2\gamma_{SV} \quad (6)$$

$$\text{Work of cohesion for a liquid: } W_{CL} = 2\gamma_{LV} \quad (7)$$

$$\begin{aligned} \text{Work of adhesion for an interface: } W_A = \\ \gamma_{SV} + \gamma_{LV} + \gamma_{SL} + \gamma_{LV}(\cos\theta + 1) \end{aligned} \quad (8)$$

where γ_{SV} , γ_{SL} , and γ_{LV} are the effective interfacial tensions between two phases, λ is the spreading coefficient for each phase which can be calculated using the following relationships [27]:

$$\lambda_{LS} = W_A - W_{CL} \quad (9)$$

$$\text{and } \lambda_{SL} = W_A - W_{CS} \quad (10)$$

The SEM micrographs with a magnification of 100X of calcium sodium aluminosilicate ceramic granules were classified by the sieve analysis, as shown in Fig.7. The granule sizes of calcium sodium aluminosilicate (75, 106, 150, and 212 μm) are uniform; the granules are of good flow property, with a dense and smooth surface. Wet granulation is used to improve flow, compressibility, bio-availability, homogeneity, electrostatic properties, and stability of solid dosage forms. There are many factors affecting the wet granulation: agglomeration, mixing, wet massing, porosity of powder, liquid bridges, coalescence, electrostatic force, chemical bonding, and etc. Other important factors of a porous-solid granule are specific surface area, moisture content, particle size distribution, particle shape, intra-granular porosity, heating, evaporation, mean granule size, apparent viscosity including gravity force during granulation process, and surface tension [22].

Comparison of TEM micrographs of calcium sodium aluminosilicate ceramic granules between the granule with the size of 75 μm with magnifications of 80,000X, 40,000X, and 25,000X (a1, a2, and a3) and the granule with the size of 212 μm with magnifications of 80,000X, 40,000X, and 25,000X (b1, b2, and b3), respectively are shown in Fig. 8. Fig. 8(b1, b2, b3) belong to the granule with the size of 212 μm showing

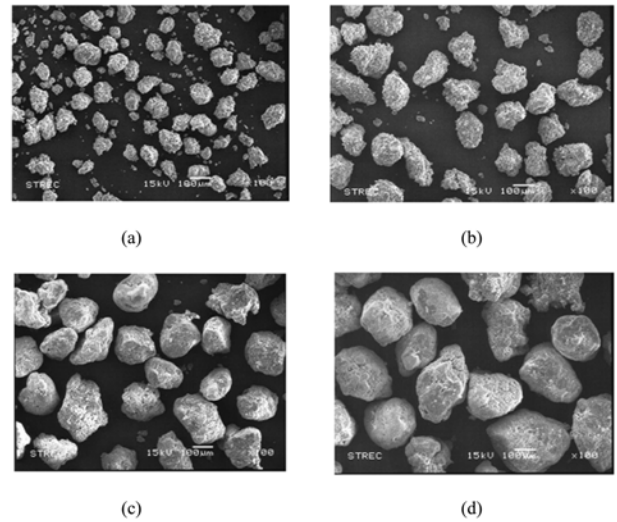


Fig. 7. SEM micrographs of calcium sodium aluminosilicate ceramic granules; (a) 75 μm , (b) 106 μm , (c) 150 μm , and (d) 212 μm .

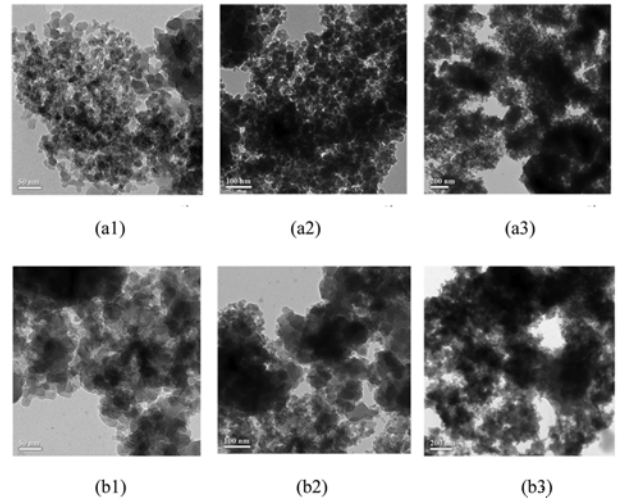


Fig. 8. TEM micrographs of calcium sodium aluminosilicate ceramic granules with the diameters; (a1) 75 μm with the magnification of 80000X, (a2) 75 μm with the magnification of 40000X, (a3) 75 μm with the magnification of 25000X, (b1) 212 μm with the magnification of 80000X, (b2) 212 μm with the magnification of 40000X, and (b3) 212 μm with the magnification of 25000X.

larger granules size than those of Fig. 8(a1, a2, a3) (75 μm). Porous-solid materials have a cohesive structure which depends on the interaction between the primary particles. The cohesive structure causes a void space which is not occupied by atoms, ions, and fine particles. However, the porous-solid materials have the inter-particle forces which are different depending on chemical bonding, van der Waal force, covalent bond, hydrogen bond, magnetic force, electrostatic force, and surface tension of the thick adsorbed layer on the particle surface. Therefore, pores within solids are classified into the intra-particle pores (called intrinsic and extrinsic intra-particle pores), the inter-particle pores called agglomeration (rigid inter-particle pore), and aggregation (flexible inter-particle pore) [28]. The

porous-solid ceramic granules obtained possess stable agglomerates. Thus, inter-particle pores have influences on stability, capacity, shape, and size according to packing of primary particles. The stability depends on the surrounding conditions, such as temperature, moisture, air velocity, pressure. Almost all inter-particle pores in agglomerates are rigid, whereas those in aggregates are flexible. Almost all sintered or calcined porous-solid materials have rigid pores due to strong chemical bonding among the particles. Therefore, the ceramic granulation prepared by the porous-solid ceramic yields mesoporosity (between 2 nm-50 nm), with sodium carboxymethyl cellulose (CMC) as secondary particles and potential utilizations as adsorbents [22, 29].

Conclusion

Sodium carboxymethyl cellulose (CMC) was used successfully as a binder or a dispersion medium, thickener, gelling agent, long-lasting adhesion, and wet attack in a solution to form calcium sodium aluminosilicate ceramic granules without any change in the ceramic powder property. CMC is non toxic, anionic, moisture absorption, and it is a colloidal binder. The obtained solid ceramic granules (calcium sodium aluminosilicate) were fabricated from biomaterials. The obtained calcium sodium aluminosilicate granules are potential candidates to be used as an adsorbent in a variety of chemical industries due to non corrosiveness, chemical stability, non toxicity, and low cost. The advantages of calcium sodium aluminosilicate ceramic granules are of good flow ability, suitable for compression, of uniform granule size, non-contaminated, and easy for phase separation. The calcium sodium aluminosilicate ceramic granule sizes depend on a variety of important parameters: the type of binder (the DS value), the binder solution concentration, the granule formation temperature, the surface preparation of ceramic particles, the particle size and shape of particles, the specific surface area and the pore size distribution of particles, the particle discharge on surface (polar and non-polar), the adhesion-cohesion force of wet agglomeration, including attractive-repulsive force between particles.

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