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DESCRIPTION

FIELD OF THE INVENTION

[0001] The present invention discloses a method for the production of activated carbons without using strong acids or strong bases or environmentally-unfriendly $ZnCl_2$. More particularly, this invention is to disclose a method enabling a synergistic activation effect at high temperatures by adding preferred combinations of chemical activation agents derived from weak acidic salts, and/or weak basic salts, and/or neutral salts, and/or compounds to achieve high surface areas, high yields, less corrosion of processing facilities, inexpensive activating agents, and improved recovery efficiency of the activating agents.

BACKGROUND OF THE INVENTION

[0002] Activated carbons are carbonaceous materials featured by a large specific surface area, typically in the range of 500-2500 m^2/g. Two methods are used in manufacturing activated carbons; activation with chemicals (called chemical activation) and activation with oxidizing gases (called physical activation). The chemical activation process to produce activated carbons normally involves: 1) formation of a mixture of carbon precursors with a chemical activation agent, 2) thermal activation by heating the mixture to high temperatures for chemical reactions between the precursor and the chemical activation agent, 3) post treatment to remove chemical residues and the moisture. The physical activation process to produce activated carbons normally involves two steps for activation: a) carbonization or pyrolysis of carbon precursors and b) activation of carbon precursors at high temperatures in carbon dioxide and/or steam environments.

[0003] There is a wide choice of carbon precursors. Commercially available activated carbons are usually derived from natural materials, such as lignite, coal and coconut shell powders. As well, petroleum pitch, agricultural wastes and wood by-products, wastes from municipal and industrial activities, bio-masses, carbon fibers, carbohydrate precursors, resins, etc., have also been used or proposed for activated carbon production.

[0004] Chemical activation agents develop pores in activated carbons by severe chemical reactions between the chemical activation agent and the carbon precursor. There is a dilemma in producing activated carbons by chemical activation. To obtain activated carbons with high surface areas (1500-2500 m^2/g), chemical activation agents are normally chosen from strong acids, such as H_2SO_4 and H_3PO_4 (as taught in U.S. Pat. No. 3,835,064 to Shinomiya et al., WO2009/011590 A1 to Richard De et al.), and/or strong bases, such as KOH (U.S. Pat. No. 7,410,510 to Fujino et al., U.S. Pat. No. 8,784,764 to Gadkaree et al.) and NaOH (U.S. Pat. No. 7,410,510 to Fujino et al., Lillo-Rodenas et al. (2001), "Preparation of activated carbons from

Spanish anthracite: II. Activation by NaOH", Carbon, 2001, 39, 751 -759.) However, such strong acids and bases can also cause severe corrosion to the processing facilities, normally made of metallic materials. This increases operational costs and reduces recovery efficiency. In addition, strong acids and strong bases are difficult to handle in their transportation and storage. The use of chemicals with weaker activation ability is usually sufficient if activated carbons with moderate surface areas (500-100 m^2/g) are to be made. For example, an activation method using less corrosive zinc chloride ($ZnCl_2$) was developed and commercialized. However, the use of $ZnCl_2$ is nowadays not recommended due to the toxicity of zinc. Potassium carbonate (K_2CO_3) has also been proposed to produce activated carbons because it is neither hazardous nor deleterious, and is frequently used as food additives; however, it has not been commercially employed for producing activated carbons, largely because of its weak ability of activation. More importantly, the use of the chemicals with weaker activation ability would also make the activated carbon with low surface areas that are less cost-effective and less competitive, as compared with those products made by physical activation.

[0005] Although physical activation is the most commonly used method in industry, the activated carbons produced by physical activation have limited surface areas, usually less than 1500 m^2/g. Recently, chemical activation agents have been added into the process of carbonization, the first step of physical activation, in a form of hybrid chemical and physical activation methods (U.S. Pat. No. 5,504,050 to Hayden et al., U.S. Pat. No. 8,709,972 to Istvan et al., U.S. Pat. No. 5, 102,855 to Greinke et al,, U.S. Pat. No. 7,541 ,312 to Dietz et al.). These hybrid methods, however, had yielded a limited increase in the surface area of activated carbons (to a value < 2500 m^2/g). In addition, strong acids added in the carbonization step would cause the corrosion of processing facilities during the second step of physical activation.

[0006] US2015/329364 discloses activated carbon products which can be made by reacting a hydroxybenzene compound and an aldehyde compound in the presence of a solvent to produce a prepolymer. The prepolymer and an additive can be reacted to produce a wet gel product that can be dried, pyrolized, and activated to produce an activated carbon product. The activated carbon product can have a specific surface area of about 100 m^2/g to about 7,000 m^2/g, a pore volume of about 0.2 cm^3/g to about 10 cm^3/g, and/or an average pore size of about 0.5 nm to about 150 nm. CN101759181 discloses a method for producing activated carbon for super capacitors and relates to activated carbon, comprising the following steps: a, selecting materials; b, steaming the materials and phosphoric acid by the weight ratio being 1: (2.5-4.0), adding phosphoric acid with the concentration thereof being 30% to 50%; c, carbonizing; d, activating; e, submerging the carbon surface and recovering the phosphoric acid from the activated material; f, pickling the material; g, dewatering, drying, pulverizing and packaging separately to obtain the finished product of activated carbon. JP2008/184359 discloses a carbide suitable for electrode material for electrical double layer capacitors superior in capacitance at low temperatures particularly among carbides obtained from polymers of resolcinols and aldehyde compounds. JPS5433293 discloses activated carbon with many fine

holes of large hole diameters, by adding specified amounts of K or Na compound as a first component and Ca compound as a second component to carbonaceous material.

[0007] Therefore, one of the objectives of the present invention is to produce activated carbons, either by chemical activation or by the hybrid chemical and physical activation, using chemical agents derived from weak acidic salts, and/or weak basic salts, and/or neutral salts, and/or compounds to avoid or minimize the issue of corrosion of processing facilities.

SUMMARY OF THE INVENTION

[0008] The invention is set out in accordance with the appended claims. The present invention discloses a method of making activated carbons with high surface areas characterised by a BET (Brunauer-Emmett-Teller) surface area, ranging from about 1000-3500 m^2/g, without using strong acids or strong bases or environmentally-unfriendly $ZnCl_2$. The present method triggers a synergistic activation effect at high temperatures by preferred combinations of chemical activation agents comprising a first salt which is potassium carbonate, potassium bicarbonate or potassium chloride and a second salt which is a phosphate. According to one embodiment the present method comprises of (a) forming a mixture of a carbon precursor with a first component comprising a first salt which is which is potassium carbonate, potassium bicarbonate or potassium chloride, and one or more second components comprising at least one second salt which is a phosphate to form a mixture; (b) preheating said mixture to a first temperature of from 150 °C to 600 °C and soaking for a period of time between 10 min to 10 h in an inert environment; and (c) activating said mixture in an inert environment by raising the temperature to a second temperature of from 600 °C to 1000 °C and soaking for a period of time between 10 min to 20 h; wherein the method is conducted without using any strong acids or strong bases or $ZnCl_2$.

[0009] It is to be understood that other aspects of the present invention will become readily apparent to those skilled in the art from the following detailed description, wherein various embodiments of the invention are shown and described by way of illustration. Accordingly the drawings and detailed description are to be regarded as illustrative in nature and not as restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] A further, detailed, description of the invention, briefly described above, will follow by reference to the following drawings of specific embodiments of the invention. The drawings depict only typical embodiments of the invention and are therefore not to be considered limiting of its scope. In the drawings:

FIG. 1a is a flow process diagram of a chemical activation method of the present invention for

making activated carbons with high surface areas;

FIG. 1b is a flow process diagram of a hybrid chemical and physical activation not according to the invention for making activated carbons with high surface areas; FIG. 2 is a graph of activation effect and yield vs. % of a second component using the results from Examples 1 -6, wherein the activation process follows the conditions described in FIG. I a;

FIG. 3a are graphs of cumulative pore volume and (inset) pore-size distribution vs. pore width of activated carbons made from an embodiment of a process with the conditions described in Example 2;

FIG. 3b are graphs of cumulative pore volume and (inset) pore-size distribution vs. pore width of activated carbons made from an embodiment of a process with the conditions described in Example 4.

FIG. 3c are graphs of cumulative pore volume and (inset) pore-size distribution vs. pore width of activated carbons made from an embodiment of a process with the conditions described in Example 8;

FIG. 3d are graphs of cumulative pore volume and (inset) pore-size distribution vs. pore width of activated carbons made from a process with the conditions described in Example 15; and

FIG. 4 is a graph of activation effect and yield vs. percentage of the second component using the results from Examples 9-14, wherein the activation process follows the conditions described in FIG. I b.

[0011] The drawing is not necessarily to scale and in some instances proportions may have been exaggerated in order more clearly to depict certain features.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The description that follows and the embodiments described therein are provided by way of illustration of an example, or examples, of particular embodiments of the principles of various aspects of the present invention. These examples are provided for the purposes of explanation, and not of limitation, of those principles and of the invention in its various aspects.

Definitions

[0013] As used herein an activated carbon shall refer to any porous carbonaceous material comprising at least 75% elemental carbon and characterized by a BET (Brunauer- Emmett-Teller) surface area of at least 500 m^2/g produced from chemical activation methods, physical

activation methods, or the hybrid chemical and physical activation methods. As used herein the term an acidic salt shall refer to a salt formed between a strong acid and a weak base. As used herein the term a basic salt shall refer to a salt formed between a weak acid and a strong base. As used herein the term a neutral salt shall refer to a salt formed between a strong acid and a strong base. As used herein the term a compound shall refer to an entity consisting of two or more different atoms which associate via chemical bonds. As used herein the term yield shall refer to the weight percentage of the resulting activated carbons to the carbon precursors used. As used herein the term micropores shall refer to the pore diameter smaller than 2 nm, characterized by the BET method and calculated by the NLDFT (non-local density functional theory) model. As used herein the term mesopores shall refer to the pore diameter between 2 nm and 50 nm, as characterized by the BET method and calculated by the NLDFT model. As used herein the term surface area shall refer to specific surface area measured as m^2/g, obtained from the BET method.

Method of Making Activated Carbons with High Surface Areas

[0014] The present invention discloses a method of making activated carbons with high surface areas, ranging from 1000-3500 m^2/g, without using strong acids or strong bases or environmentally-unfriendly chemicals such as $ZnCl_2$. The high surface area achieved from the present invention is possible because of a synergistic activation effect. The present inventors have surprisingly found that this synergistic activation is triggered at high temperatures by adding a preferred combination of chemical activation agents derived from the group consisting of weak acidic salts, weak basic salts, neutral salts, preferred compounds. In one embodiment, described in FIG. Ia., categorized as chemical activation, the present method comprises of (a) forming a mixture of a carbon precursor with a first component comprising a first salt which is which is potassium carbonate, potassium bicarbonate or potassium chloride and one or more second components comprising at least one second salt which is a phosphate, and optionally containing a binder; and (b) activating said mixture by raising the temperature to a second higher temperature and soaking for a predetermined period of time in an inert environment. The process further involves preheating said mixture to a first, intermediate temperature and soaking, or maintaining the mixture at the intermediate temperature, for a predetermined period of time in an inert environment prior to activating the mixture.

[0015] Referring now to step 4 of mixing in FIG. Ia, there is no limitation to the mixing method in this invention. However, dry mixing through a dual shaft mixer is preferred. In some embodiments, the carbon precursor 3, the first component 1, and at least one second component 2 may be pulverized or ground into particles having an average size less than 5 mm before dry mixing.

[0016] The avoidance of using strong acids, such as H_2SO_4 and H_3PO_4, or strong bases, such as KOH and NaOH, or environmentally-unfriendly chemicals, e.g., $ZnCl_2$, to produce activated

carbons with high surface areas is advantageous in the following three aspects 1) the corrosion of the processing facilities has been minimized; 2) the cost of activating agents has been reduced since weaker activating agents are commonly less expensive, more dilute and safer to transport etc.; 3) the recovery efficiency of the activating agents used has been improved.

[0017] Recovery efficiency of the present activating agents is improved since corrosion is reduced, which in turns ensures that less of the activating agent is consumed in side corrosion reactions between the agents and the equipment. Therefore, more elements from the agents are maintained in the carbon materials to be recovered.

[0018] The present invention also sets no limitation to the type of carbon precursors 3 used in the process. The carbon precursors fit for in this method include, but not limited to, petroleum pitch; coconut shell powders; lignite or coal; municipal wastes and industrial by-products, including waste newspaper, waste tires, refuse derived fuel, PET bottle, waste carbon slurries and blast furnace slag, asphaltenes, biological wastes generated during lactic acid fermentation from garbage, and sewage sludge; bio-masses; agricultural wastes, including coir pith, bagasse, sago waste, banana pith, maize straw, silk cotton hull and maize cob, rice husk, rice hulls; fruit stones, including nutshells, olive stone, macadamia nuts, pecan shell, vetiver roots, and cassava peel; wood by-products, including coconut tree sawdust, bamboo, pinewood, sawdust; carbon fibers; vegetal origin, including seed fibers, bast fibers, leaf fibers, fibers from fruits, artificial fibers from cellulose, viscose, cuppramonium rayons and PVA fibers; carbohydrate precursors, including sucrose, lactose, starch, corn syrup, cellulose; resins, including polystyrenedivinylbenzene ion exchange resin, phenol-formaldehyde resin; and combinations thereof. In some embodiments, organic wastes are the preferred carbon precursors for this method. In another embodiment, coconut shells are the preferred carbon precursors for this method.

[0019] According to one embodiment, for example, the alkali salt is preferably potassium carbonate. In another embodiment, potassium bicarbonate is a preferred alkali salt. In another embodiment, potassium chloride is a preferred alkali salt.

[0020] Of the second component 2 one or more second salts are phosphates.

[0021] The present mixture in step 4 may optionally comprise a binder. Examples of binders include, but are not limited to, cellulosic binders including methylcellulose, ethylcellulose, hydroxybutylcellulose, hydroxybutylmethylcellulose, hydroxyethylcellulose, hydroxymethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, hydroxyethylmethylcellulose, and sodium carboxylmethyl cellulose; resinous binders including polyvinylidene chloride, polyvinyl chloride, polyvinyl alcohol, resole, novolac resins; bitumen, asphaltenes, and starch. The present invention differs from the prior art (for example, WO2009/011590 A1 to Richard De et al., U.S. Pat. No. 7,541,312 B2 to Dietz et al., U.S. Pat. No. 3,835,064 to Shinomiya et al., WO 2007/114849 A2 to Buiel et al., U.S. Pat. No. 5, 102,855 A to Greinke et al.) in the avoidance of using strong acids, such as H_2SO_4 and H_3PO_4, or

strong bases, such as OH and NaOH, or environmentally-unfriendly chemicals, e.g., $ZnCl_2$, to produce activated carbons with high surface areas. In addition to advantages discussed above, strong acids and strong bases are difficult to handle in their transportation and storage. In one embodiment, the corrosion rate caused by the mixture of first salt 1 and second salt and/or compound 2 together is only 1/1000 of that caused by KOH. In another embodiment, dehydrating agents which can also be corrosive may be excluded from the mixtures (either excluded from the first component 1 or from the second component 2) to reduce the corrosion attack.

[0022] The present invention further differs from the prior art (for example, U.S. Pat. No. 7,541 ,312 B2 to Dietz et al., U.S. Pat. No. 3,835,064 to Shinomiya et al., WO2007/114849 A2 to Buiel et al., U.S. Pat. No. 5,102,855 A to Greinke et al., U.S. Pat. No. 8,709,972 B2 to Istvan et al., E.P. Pat. No. 2,478,957 A1 to Reimerink-Schats et al., U.S. Pat. No. 3,876,451 A to Zall et al., U.S. Pat. No. 5,504,050 to Hayden et al.) in triggering a synergistic activation effect at high temperatures from a preferred combination of a first component comprising a first salt 1 and one or more second components 2 selected from at least one second salt, a compound and combinations thereof, to produce microporous activated carbons with high surface areas and high yields. The synergistic activation effect is apparent in FIG. 2. Referring now to FIG 2, also shown in Examples 1 -6, the surface areas of activated carbons activated from only first salt 1 (1100 m^2/g) or only second salt 2 (200 m^2/g) are much lower than those activated from the mixtures of both (3206 m^2/g). The latter is almost triple the sum of the surface areas from the former two cases, indicating a strong synergistic enhancement in surface area. As discussed in Example 3 below, the yield of activated carbons with the surface area of >3000 m^2/g produced from the present invention is 20 wt%, much larger than that of activated carbons produced from a strong base, KOH, 8 wt% (Example 7). In one embodiment, the yield of activated carbons with a surface area of >2000 m^2/g produced from the present invention is 40-45 wt% (Example 8).

[0023] The present method further comprises (c) activating said mixture by raising the temperature to a second higher temperature and soaking for a predetermined period of time in an inert environment. The chemical activation takes place in step 6, wherein the activation temperature is in the range of 600 °C to 1000 °C, preferably, in the range of 700 °C to 900 °C. The soaking periods at the activation temperature are in the range of less than 10 min to 20 h, preferably, in the range of 0.2 h to 6 h. There are no additional chemical agents added in step 6. The pressure in the reactor controlled during this step is in the range of 0.01 Torr to 10^4 Torr (1.3 Pa to 1.3 MPa).

[0024] The present method further comprises preheating 5 said mixture to a first, intermediate temperature and soaking for a predetermined period of time in an inert environment, prior to activating. The intermediate temperatures in preheating step 5 are in the range of 150 °C to 600 °C. The soaking period of time at the intermediate temperature is in the range of less than 10 min to 10 h, preferably, in the range of 0.2 h to 6 h. The pressure in the reactor controlled

during this step is preferably in the range of 0.01 Torr to 10^4 Torr (1.3 Pa to 1.3 MPa)

[0025] Exemplary inert atmospheres in steps 5 and 6 may include at least one selected from nitrogen, argon, and the noble gases. Steps 5 and 6 are typically carried out in a furnace capable of attaining the high temperatures required. The examples of the furnaces are, but not limited to, tube furnaces, rotary furnaces, and belt furnaces. In one embodiment, a fluidized bed reactor is used in this method to conduct step 5 and step 6, wherein the preheating and the activation parameters may need to adjust accordingly. In another embodiment, a microwave is used in this method to conduct step 5 and step 6, wherein the preheating and the activation parameters may need to adjust accordingly. All equipment that can be used to provide energy or temperature to trigger the synergistic activation effect and conduct the chemical activation is also within the scope of in the present invention. In one embodiment, step 7 of post treatment in FIG. la may comprise, but not limited to, washing, drying, and pulverization.

[0026] In FIG. la, step 8 is the recycle of the first component 1 and/or the second component 2. Since little to no amount of the first and second components is consumed by corrosion activity, corrosion of the processing facilities has been minimized and recycles of the first component 1 and/or the second component 2 may achieve a very high percentages. In one embodiment, the recovery efficiency can achieve about 90% of the first component 1, and about 80% of the second component 2.

[0027] The present disclosure includes micropore-dominant activated carbons made according to the methods recited hereinabove. Micropore-dominant activated carbons are characterized as having a high surface area between about 1000 m^2/g and about 3500 m^2/g, preferably, above about 2000 m^2/g; a yield between 8 wt% and 50 wt% based on the initial weight of the carbon precursor, preferably, in the range of about 15 wt% to about 40 wt%.

[0028] In FIG. la, activation carbons 9 are micropore-dominated activated carbons with the volume percentage of micropores (<2 nm) being in the range of about 50% to about 85%, the volume percentage of mesopores (2~50nm) being in the range of about 15% to 50%. It is further possible by methods of the present invention to adjust pore structure (pore size distribution) by changing 1) the ratios of any one of the carbon precursor 3 to first component 1 ; the first component 1 to the second component 2; and/or the carbon precursor 3 to the second component 2; 2) the activation temperature; 3) the type of carbon precursor.

[0029] FIG. 3a, FIG. 3b derived from Examples 2 and 4 show that the average pore size is increased by increasing the ratio of the carbon precursor 3 to the first component 1. When the ratio is 2 to 0.9, over 55% of pores are micropores and around 23% of pores are in the range of 2 nm to 4 nm. When the ratio is between 2 to 5.43, over 50% of pores are micropores and around 49% of pores are in the range of 2 nm to 4nm. The pore structure is also dependent on the type of carbon precursors used in this method. As shown in FIG. 3c and Example 8, when asphaltenes were used as carbon precursors, the obtained activated carbons possess over

83% micropores and around 17% mesopores. This pore structure is very different from that obtained when coconut shells were used as carbon precursors, as shown in FIG. 3a and FIG. 3b.

[0030] Referring now to FIG. lb, which shows a method not according to the invention, said first component 1, said second component 2, said carbon precursors 3, and said mixing step 4 are described in FIG. la. The synergistic activation effect at high temperatures is again triggered from using a preferred combination of a first component 1 and at least one second component 2 in this hybrid chemical and physical activation method. In this hybrid activation method, the amount of the components used is lower than that used in the pure chemical activation method as shown in FIG. la and described in Examples 9- 14.

[0031] The present hybrid method preferably further comprises preheating said mixture to a first, intermediate temperature and soaking for a preset period in an inert environment. The intermediate temperatures in step 15 are in the range of 200 °C to 1000 °C. The soaking periods at the intermediate temperature are in the range of less than 10 min to 10 h, preferably, in the range of 0.2 h to 6 h. The pressure in the reactor controlled during this step is in the range of 0.01 Torr to 10^4 Torr (1.3 Pa to 1.3 MPa).

[0032] Exemplary inert atmospheres for step 15 may include at least one selected from nitrogen, argon, and the noble gases.

[0033] The present method further comprises (c) activating said mixture by raising the temperature to a second, higher temperature and soaking for a predetermined period of time under an oxidizing environment. The activation takes place in step 16, wherein the oxidizing environment comprising at least one oxygen-containing component selected from the group consisting of carbon dioxide, air, steam and mixtures thereof. The activation temperature in step 16 is in the range of 800 °C to 1200 °C, preferably, in the range of 900 °C to 1100 °C. The soaking periods at the activation temperature are in the range of less than 10 minutes to 20 h, preferably, in the range of 0.2 h to 6 h. The pressure in the reactor controlled during this step is in the range of 0.01 Torr to 10^4 Torr (1.3 Pa to 1.3 MPa).

[0034] Step 16 and optional step 15 are typically carried out in a furnace capable of attaining the high temperatures required. The examples of the furnaces are, but not limited to, tube furnaces, rotary furnaces, and belt furnaces. Optionally, a fluidized bed reactor is used in this method to conduct steps 15 and 16, wherein the preheating and activation parameters may need to adjust accordingly. Optionally, a microwave is used in this method to conduct steps 15 and 16, wherein the preheating and activation parameters may need to adjust accordingly. All equipment that can be used to provide energy or temperature to trigger the synergistic activation effect and conduct the chemical activation is not according to the present invention.

[0035] Optionally, step 7 of post treatment in FIG. lb may comprise, but not limited to, washing, drying, and pulverization.

[0036] In FIG. Ib, step 8 is recycle of the first component 1 and/or the second component 2. Optionally, the recovery efficiency can achieve 90% recover of the second component 2, and 90% recover of the first component 1.

[0037] In FIG. Ib, activation carbons 19 are microporous activated carbons with the volume percentage of micropores (<2 nm) being in the range of 50% to 85%, the volume percentage of mesopores (2~50nm) being in the range of 15%> to 50%. The present invention has another advantage that the pore structure (pore size distribution) is able to be adjusted by changing 1) the ratios of any one of the carbon precursor 3 to first component 1 ; the first component 1 to the second component 2; and/or the carbon precursor 3 to the second component 2; 2) the activation temperature; 3) the type of carbon precursor. Optionally, the pore structure is also dependent on the type of carbon precursors used in this method, as shown in FIG. 3d and described in Example 15, wherein over 83% of pores are micropores and around 15% of pores are in the range of 2 nm to 4 nm when asphaltenes were used as carbon precursors.

[0038] The synergistic activation effect of the present methods is apparent in FIG. 4. Referring now to FIG 4, also as described in Examples 9-14 which do not fall within the scope of the claims, the surface areas of activated carbons activated by adding first salt 1 only (900 m^2/g) or second salt 2 only (1236 m^2/g) are much lower than those activated by adding the mixtures of both (2648 m^2/g). The latter is also higher than the sum of the surface areas from the former two cases, indicating a strong synergistic enhancement in surface area. Optionally, the yield of activated carbons with a surface area of > 1700 m^2/g produced from the present invention is 50-55 wt%, based on the initial weight of the carbon precursor (Example 15). In another embodiment, dehydrating agents may be excluded from the mixtures (either excluded from the first component 1 or from the second component 2) to minimize the corrosion attack.

[0039] The present methods provide a cost-effective method to produce activated carbons with high surface areas. The present invention, in its capability of adjusting the pore structures, makes the resulting microporous activated carbons potential to be used in applications, but not limited to, ultracapacitors, batteries, fuel cells, water treatment and purification, air/gas treatment or purification, gold recovery, mercury removal, medical uses, cosmetics, and catalyst supporters.

[0040] In the case of ultracapacitors for example, using the present activated carbons with a surface area of about 2700 m^2/g, and an apparent density of about 0.22 g/cc, the capacitance of an electrode tested in the form of 50 F full pouch cells using a commercial organic electrolyte of 1 mol/L Tetraethylammonium Tetrafluoroborate (Et_4NBF_4) in Acetonitrile (AN) is between 180 F/g and 200 F/g, much higher than the capacitance of 100-130 F/g more commonly seen in commercial ultracapacitors. Using the present activated carbons with a surface area of about 2400 m^2/g, and an apparent density of >0.26 g/cc, the capacitance of the electrode tested in the form of 50 F full pouch cells using the commercial organic

electrolyte of 1 mol/L Et4NBF4in AN is between 150 F/g and 170 F/g. This shows a full-cell performance improvement of about 20% in terms of volumetric and gravimetric performance as compared to commercial ultracapacitors. Furthermore, since the present method produces activated carbons with high purity, high cycling performance in the order of around 1 million cycles has also been observed for ultracapacitor electrodes made from the present activated carbons.

[0041] In the case of lithium-sulfur batteries for example, sulfur can be impregnated into activated carbons. Using the present activated carbons having a surface area of about 3000 m^2/g as the sulfur cage, sulfur loading in the resulted carbon-sulfur compound can reach 80 wt%. Furthermore, the present activated carbon when used as a cage also protects the embedded sulfur from dissolving into the electrolyte, which improves the cycle life of lithium-sulfur batteries. The present activated carbons can also be used in hybrid supercapacitors and compared to lithium-ion anodes and/or lithium-ion cathodes and/or NiOOH, for example to improve the capability of ion adsorption in the batteries. The present activated carbons can further be used as an additive in electrodes in various batteries to improve rate capabilities, including lithium-ion batteries, lithium-air batteries, Ni-H, Ni-Cd, Ni-Zn, Lead-acid batteries, among others.

[0042] In the case of water treatment and purification, air/gas treatment or purification, cosmetics, gold recovery, mercury removal for example, the present activated carbons have very large surface areas and controllable pore size to adsorb/absorb harmful organic or gaseous molecules or metallic elements. In addition, the present group of activated carbons can be used as catalyst supporters to carry a large amount of catalyst nanoparticles in these applications for chemical adsorption/conversion of harmful substances. Similar usage of activated carbons can also be applied to medical uses and fuel cells. For example, using activated carbon as catalyst supporters for enhanced chemical reactions.

[0043] Although the particular methods herein shown and described in detail are capable of achieving the above described objectives of the invention, it is understood that the description and drawings presented herein represent some, but not all, embodiments that are broadly contemplated. Methods that are disclosed may thus comprise variations other than those disclosed.

[0044] The preheating step may be made up of multistage preheating steps. Step 5/15 in FIG. 1 may be conducted at a reduced pressure than those previously listed, in the reaction chamber, e.g., in a furnace.

EXAMPLES

[0045] The present invention will be described in further detail below through working examples.

Examples 1-6

[0046] Activated carbons with high surface areas were produced using chemical activation with and without a synergistic activation effect being triggered. Coconut shell (2 g), trisodium phosphate (1.62 g), and potassium bicarbonate (3.62 g) were pulverized and dry mixed at ambient temperature in Example 1. In Examples 2-4, the amount of potassium bicarbonate was changed to 0.9 g, 1.81 g, 5.43 g, respectively, while others were maintained the same. In order to prove the synergistic activation effect, the comparative Examples 5 and 6 were also conducted, wherein potassium bicarbonate was 0 g but trisodium phosphate was 1.62 g in Example 5, and trisodium phosphate was 0 g but potassium bicarbonate was 3.62 g in Example 6, while coconut shell was maintained at 2 g. In all 6 examples, the mixtures were preheated to 200°C for 1 h and immediately activated at 800°C for 1 h in nitrogen-protected environment. The temperature was then cooled to ambient temperature within 5 h. During the whole process, the nitrogen gas flow rate was controlled at 1 oven vol/h. The activated mixtures were washed and dried to obtain activated carbons. The BET surface area and the yield of the activated carbons in 6 examples are listed in Table 1 and also shown in FIG. 2.

TABLE 1

Surface Area and Yield of Activated Carbon Made with and without the Synergistic Activation Effect					
Example	Coconut Shell	Potassium Bicarbonate	Trisodium Phosphate	Surface Area	Yield
1	2g	3.62 g	1.62 g	3206 m^2/g	16 wt%
2	2g	0.9 g	1.62 g	2765 m^2/g	20 wt%
3	2g	1.81 g	1.62 g	2954 m^2/g	19 wt%
4	2g	5.43 g	1.62 g	3029 m^2/g	13 wt%
5	2 g	0 g	1.62 g	200 m^2/g	40 wt%
6	2 g	3.62 g	0 g	1100 m^2/g	22 wt%

[0047] As seen in Table 1 and FIG. 2, the synergistic activation effect was triggered as long as both potassium bicarbonate in first salt 1 and trisodium phosphate in second salt 2 were added together to the mixtures. The BET surface area can be improved to 3206 m^2/g at the optimized ratio among coconut shell, potassium bicarbonate, and trisodium phosphate. Without adding either potassium bicarbonate or trisodium phosphate, the surface area is much lower.

Comparative Example 7

[0048] Coconut shell (2 g) and potassium hydroxide (2 g) were pulverized and dry mixed at

ambient temperature in Comparative Example 7. All the following activation and post treatment steps are the same as Examples 1 -6. The resulting activated carbon has a BET surface area of 3 146 m^2/g and a yield of 8 wt%.

Comparative Example 8

[0049] Asphaltenes in solids (2 g), trisodium phosphate (1.62 g), and potassium bicarbonate (3.62 g) were pulverized and dry mixed at ambient temperature in Comparative Example 8. All the following activation and post treatment steps are the same as Examples 1-6. The resulting activated carbon has a BET surface area of 2009 m^2/g and a yield of 42 wt%.

Examples 9-14 (not within scope of claims)

[0050] Activated carbons with high surface areas were produced using hybrid chemical and physical activation with and without synergistic activation effect being triggered. Coconut shell (2 g), trisodium phosphate (1.13 g), and potassium chloride (1.90 g) were pulverized and dry mixed at ambient temperature in Example 9. In Examples 10-12, the amount of potassium chloride was changed to 0.48 g, 0.95 g, 2.86 g, respectively, while others were maintained the same. In order to prove the synergistic effect, the comparative Examples 13 and 14 were also conducted, wherein potassium chloride was 0 g but trisodium phosphate was 1.13 g in Example 13, and trisodium phosphate was 0 g but potassium chloride was 1.90 g in Example 14, while coconut shell was maintain at 2 g. In all 6 examples, the mixtures were preheated to 700 °C for 2 h in nitrogen-protected environment and activated at 1000 °C for 2 h in carbon dioxide environment. The temperature was then cooled to ambient temperature within 5 h in nitrogen-protected environment. During the process, the nitrogen gas flow rate was controlled at 1 oven vol/h, and the carbon dioxide gas flow rate was controlled at 1 oven vol/h. The activated mixtures were washed and dried to obtain activated carbons. The BET surface area and the yield of the activated carbons in 6 examples are shown in Table 2 and also in FIG. 4.

TABLE 2

Surface Area and Yield of Activated Carbon Made with and without the Synergistic Activation Effect					
Example	Coconut Shell	Potassium Bicarbonate	Trisodium Phosphate	Surface Area	Yield
1	2g	1.90 g	1.13 g	2648 m^2/g	24 wt%
2	2g	0.48 g	1.13 g	2025 m^2/g	28 wt%
3	2g	0.95 g	1.13 g	2164 m^2/g	25 wt%
4	2g	2.86 g	1.13 g	2549 m^2/g	22 wt%
5	2 g	0 g	1.13 g	1236 m^2/g	26 wt%

Surface Area and Yield of Activated Carbon Made with and without the Synergistic Activation Effect					
Example	Coconut Shell	Potassium Bicarbonate	Trisodium Phosphate	Surface Area	Yield
6	2 g	1.90 g	0 g	900 m^2/g	42 wt%

[0051] As seen in Table 2 and FIG. 4, the synergistic activation effect was triggered as long as both potassium chloride in first salt 1 and trisodium phosphate in second salt 2 were added together to the mixtures. The BET surface area can be improved to 2648 m^2/g at the optimized ratio among coconut shell, trisodium phosphate, and potassium chloride. Without adding either trisodium phosphate or potassium chloride, the surface area is much lower.

Comparative Example 15

[0052] Asphaltenes in solids (2 g), trisodium phosphate (1.13 g), and potassium chloride (1.90 g) were pulverized and dry mixed at ambient temperature in Comparative Example 15. All the following activation and post treatment steps are the same as Examples 9-14. The resulting activated carbon has a BET surface area of 1712 m^2/g and a yield of 54 wt%.

[0053] The previous description of the disclosed embodiments is provided to enable any person skilled in the art to make or use the present invention.

REFERENCES CITED IN THE DESCRIPTION

Cited references

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

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- US8709972B [0005]
- US5102855A [0005] [0022]
- US7541312B [0005]
- US2015329364A [0006]
- CN101759181 [0006]
- JP2008184359A [0006]
- JPS5433293B [0006]
- US7541312B2 [0021] [0022]
- WO2007114849A2 [0021] [0022]
- US5102855AA [0021]
- US8709972B2 [0022]
- EP2478957A1 [0022]
- US3876451A [0022]

Non-patent literature cited in the description

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Krav:

1. Fremgangsmåde til fremstilling af aktiverede kulstoffer med overfladearealer karakteriseret af et BET (Brunauer-Emmett-Teller) overfladeareal på mellem 1000 m^2/g og 3500 m^2/g, nævnte fremgangsmåde omfatter trinene:
   (a) at blande et carbonudgangsstof med en første komponent omfattende et første salt, som er kaliumcarbonat, kaliumbicarbonat eller kaliumchlorid, og én eller flere anden komponenter omfattende mindst ét andet salt, som er et phosphat, for at danne en blanding;
   (b) at forvarme nævnte blanding til en første temperatur på fra 150 °C til 600 °C og at udbløde i et tidsrum på mellem 10 minutter og 10 timer i et inert miljø;
   (c) at aktivere nævnte blanding i et inert miljø ved at hæve temperaturen til en anden, højere, temperatur på fra 600 °C til 1000 °C og at udbløde i et tidsrum mellem 10 minutter til 20 timer;
   hvori fremgangsmåden udføres uden brug af stærke syrer eller stærke baser eller $ZnCl_2$.

2. Fremgangsmåde ifølge krav 1, som yderligere omfatter at blande et bindemiddel til carbonudgangsstoffet i blandingstrinet.

3. Fremgangsmåde ifølge krav 1, hvori carbonudgangsstoffet er valgt fra gruppen bestående af petroleumsbeg; kokosskalpulvere; lignit eller kul; kommunalt affald; industrielle biprodukter; asfaltener; biologisk affald; organisk affald; biomasser; landbrugsaffald; træbiprodukter; frugtskaller; nøddeskaller; kulfibre; syntetiske polymerer; kulhydrater; resiner; og kombinationer deraf.

DRAWINGS

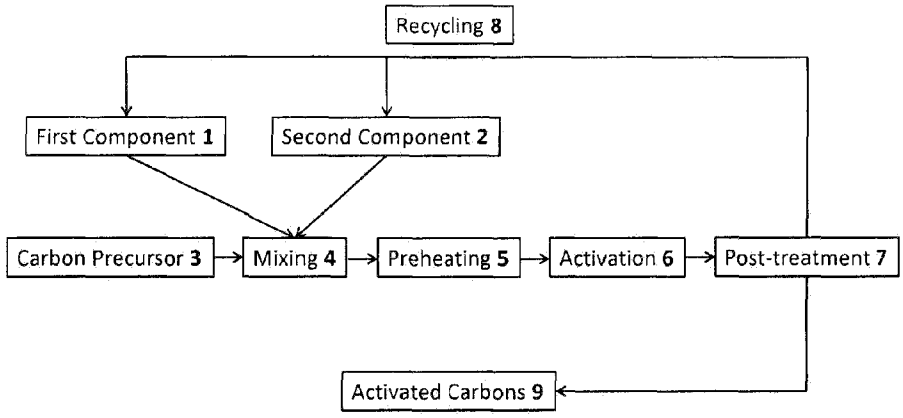


FIG. 1*a*

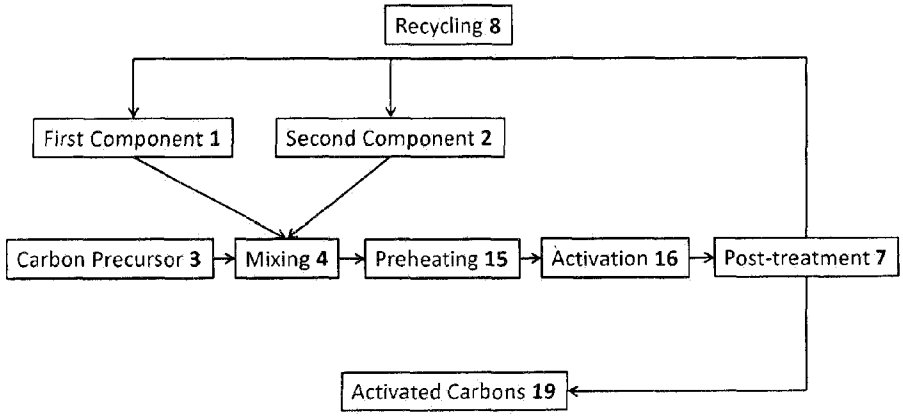


FIG. 1*b*

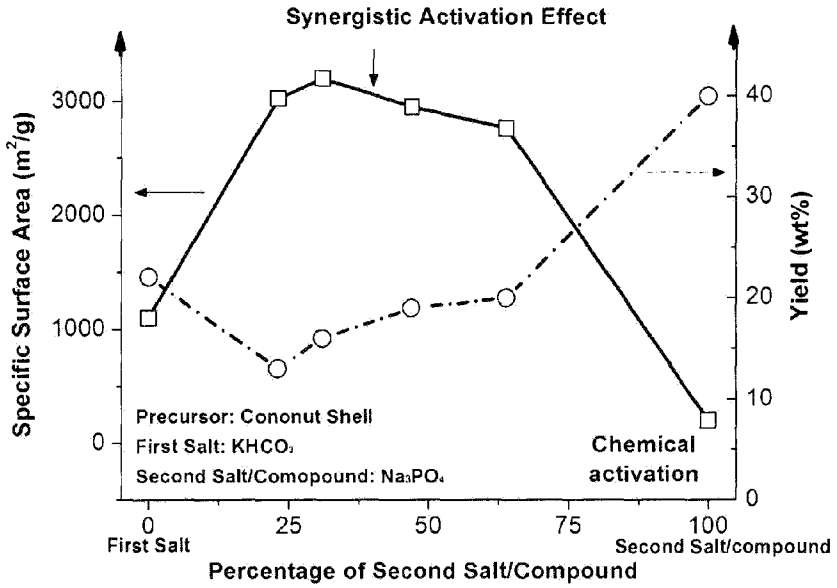

Synergistic Activation Effect
Specific Surface Area (m^2/g)
Yield (wt%)
3000
2000
1000
0
40
30
20
10
0
Precursor: Cononut Shell
First Salt: $KHCO_3$
Second Salt/Comopound: Na_3PO_4
Chemical activation
0
25
50
75
100
First Salt
Second Salt/compound
Percentage of Second Salt/Compound

FIG. 2

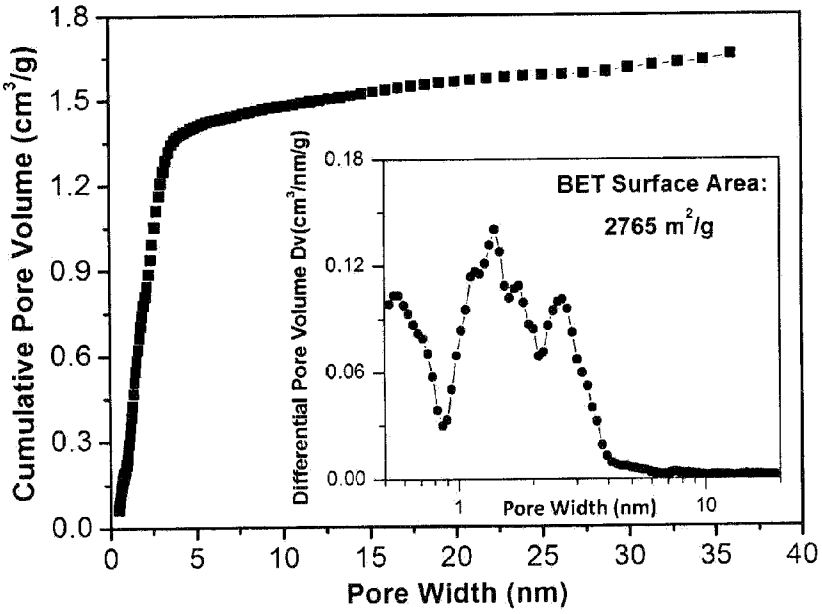

Cumulative Pore Volume (cm³/g)
Pore Width (nm)
Differential Pore Volume Dv(cm³/nm/g)
Pore Width (nm)
BET Surface Area:
2765 m²/g

FIG. 3*a*

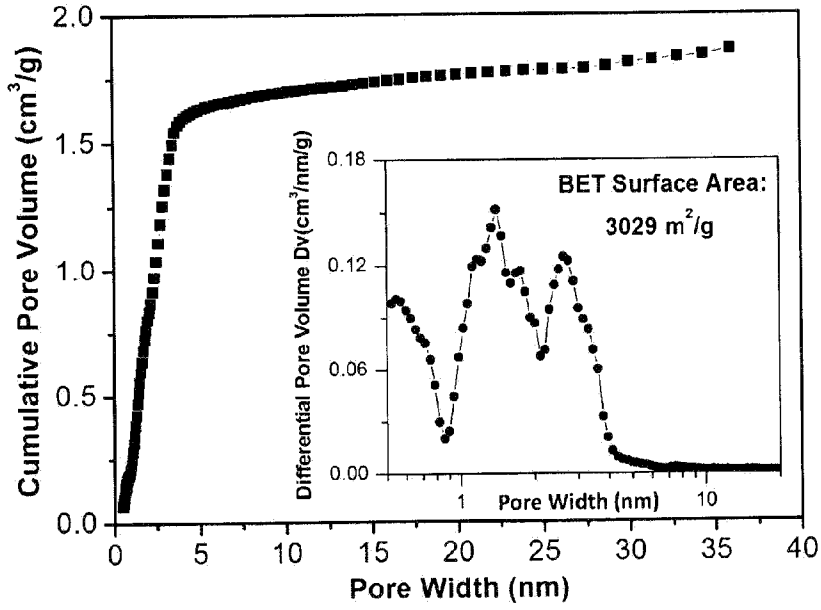

Cumulative Pore Volume (cm³/g)
Pore Width (nm)
Differential Pore Volume Dv(cm³/nm/g)
Pore Width (nm)
BET Surface Area:
3029 m²/g

FIG. 3*b*

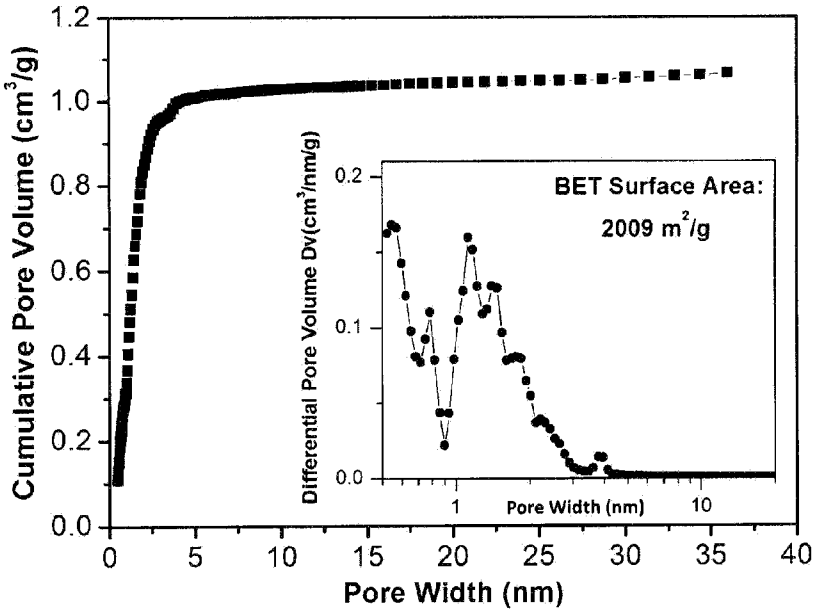

Cumulative Pore Volume (cm³/g)
Pore Width (nm)
Differential Pore Volume Dv(cm³/nm/g)
BET Surface Area:
2009 m²/g
Pore Width (nm)

FIG. 3*c*

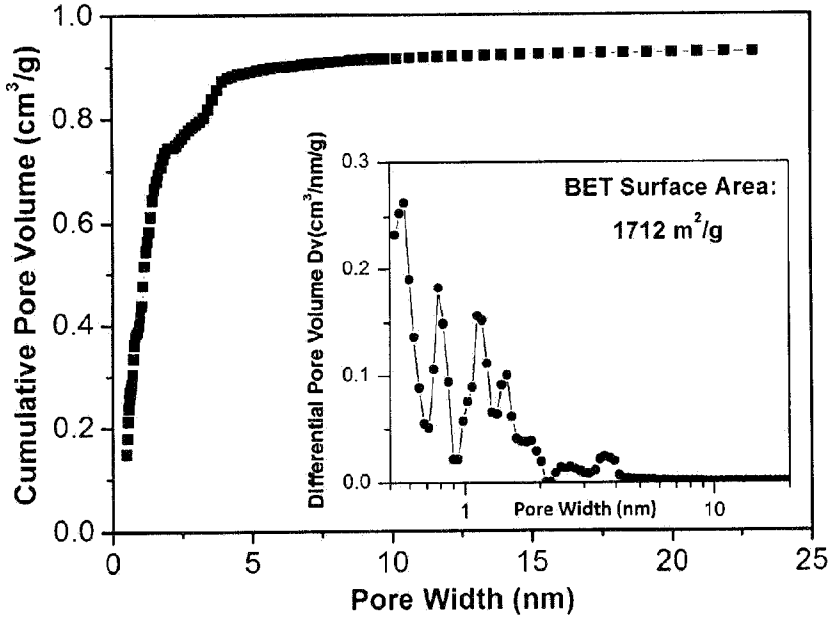

Cumulative Pore Volume (cm³/g)
Pore Width (nm)
Differential Pore Volume Dv(cm³/nm/g)
BET Surface Area:
1712 m²/g
Pore Width (nm)

FIG. 3*d*

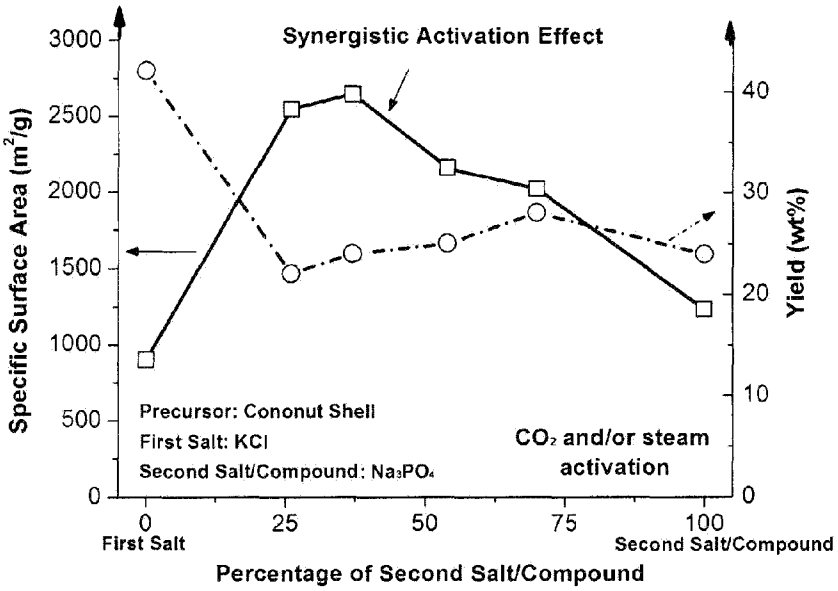

Synergistic Activation Effect
Specific Surface Area (m^2/g)
Yield (wt%)
3000
2500
2000
1500
1000
500
0
40
30
20
10
0
Precursor: Cononut Shell
First Salt: KCl
Second Salt/Compound: Na_3PO_4
CO_2 and/or steam activation
0
25
50
75
100
First Salt
Second Salt/Compound
Percentage of Second Salt/Compound

FIG. 4