(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 May 2020 (22.05.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/101972 A1

(51) International Patent Classification:
B01J 37/08 (2006.01) *B01J 37/02* (2006.01)
B01J 37/00 (2006.01) *B01J 35/00* (2006.01)
B01J 21/18 (2006.01) *C01B 32/30* (2017.01)
B01J 23/50 (2006.01) *C01B 32/312* (2017.01)
B01J 35/02 (2006.01) *C01B 32/318* (2017.01)
B01J 35/10 (2006.01) *C07C 5/02* (2006.01)

(21) International Application Number:
PCT/US2019/060041

(22) International Filing Date:
06 November 2019 (06.11.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/758,732 12 November 2018 (12.11.2018) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,

WO 2020/101972 A1

(54) Title: CATALYST SUPPORT COMPRISING MESOPOROUS CARBON

FIG. 1A

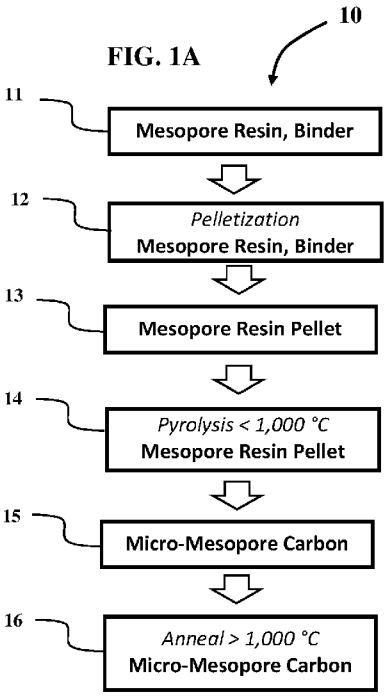
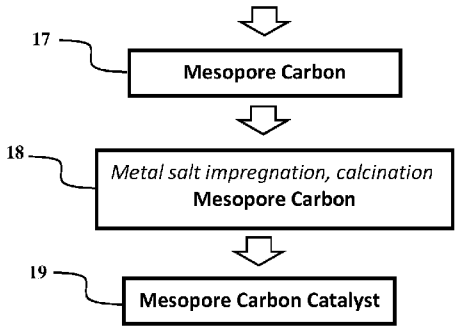


FIG. 1B



(57) **Abstract:** A carbon composition used for preparing a catalyst support structure including an admixture of: (a) a mesoporous material having mesoporous particles; and (b) a macro-molecule carbon forming binder; a process for producing the carbon composition; a carbon support structure; a process for producing the carbon support structure; a multi-metallic catalyst including (A) an annealed pyrolyzed carbon structure having an enhanced mesoporosity and mesopore size; and (B) at least two or more metallic particles disposed throughout the mesoporosity of the annealed pyrolyzed carbon structure; and a process for producing the multi-metallic catalyst.

[Continued on next page]

OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

CATALYST SUPPORT COMPRISING MESOPOROUS CARBON

FIELD

The present invention relates to (i) a mesoporous carbon resin composition, (ii) a mesoporous carbon support member made using the mesoporous carbon resin composition, and (iii) a mesoporous catalyst product or article made using the mesoporous carbon support member.

BACKGROUND

Carbon support members, for use in making a catalyst by impregnating the carbon support member with catalytic active metal particles, are known in the art. The known carbon support members usually have pores in the micropore and the mesopore size range. A carbon support member having an optimum mesoporosity is highly desirable in the catalyst industry because the mesopores of the carbon support member allow the impregnation of bimetal or multi-metal particles into the carbon support member wherein the impregnation sufficiently disperses and deposits particles into the mesoporous of the carbon support member to maximize the concentration of the bimetal or multi-metal particles in the mesopores of the carbon support member to form a catalyst product or article.

Activated carbon is traditionally produced from coal or biomass; and the carbon is activated by steam or chemicals to generate the porosities in the carbon; and then the carbon can be granulated/extruded with an additional binder to make pellets. For example, such prior processes are described in JP52008277B; and EP0831058A1.

The above-described traditional activated carbon process known in the art has several problems: (1) the raw materials are not consistent, and such non-consistency results in the production of a product having non-uniform product qualities; (2) impurities present in the natural raw materials get passed onto the final carbon product; and (3) the use of the blunt chemical/steam activation process generates complex micropore-mesopore structures in the carbon product, which causes the production of a non-uniform catalyst composition.

U.S. Patent No. 9,579,627B2 discloses a process to form microporous carbon pellets from a cation exchange resin and a carbon forming binder. The above patent describes using carbon molecular sieve pellet compositions for C2-C3 alkane/alkene

separations. Because the process of the above patent uses consistent and pure quality of starting raw materials, the resultant carbon pellets product made from the process can solve problems (1) and (2) described above for the process which uses a conventional activated carbon. However, U.S. Patent No. 9,579,627B2 does not address problem (3) described above related to the production of a non-uniform catalyst composition. The carbon pellets disclosed in the above patent are pyrolyzed at an intermediate temperature, for example, in the range of from 750 degrees Celsius (°C) to 1,000 °C; and the pyrolysis results in carbon pellets containing micropores having a micropore area, for example, of from 100 meters squared per gram (m^2/g) to 400 m^2/g. And, the carbon pellets produced by the process disclosed in the above patent lack mesopores because the process uses a gel-type (non-porous) resin precursor.

While the use of a cation exchange resin-derived mesoporous carbon, as disclosed in U.S. Patent No. 9,579,627B2, has found some success in providing a mesoporous carbon support member for a catalyst, the mesoporous carbon produced by the prior art process has two disadvantages: (1) the area of mesoporosity of the mesoporous carbon is generally small (e.g., less than (<) 30 m^2/g) and the small mesoporosity area of the mesoporous carbon limits the concentration of bimetal or multi-metal particles that can be dispersed into the mesoporous carbon; and (2) the pyrolysis of a cation exchange resin generates SO_2 and SO_3 gases, and such generation of gases needs to be controlled which makes the process complex and expensive.

Also known in the prior art are processes that use a formaldehyde carbon material, such phenol formaldehyde carbon material, to form a porous carbon. Processes that use a formaldehyde carbon material are described, for example, in Thrupore, http://www.thrupore.com/innovation.html; and Energ2, http://www.energ2.com/products.html. Typically, a phenol formaldehyde is used by carbon manufactures to make pure carbons with different pore size distributions for various applications. However, the above known prior art processes that use a phenol formaldehyde carbon material, are usually (1) pyrolyzed at an intermediate temperature (e.g., < 1,000 °C); and/or (2) activated by steam or CO_2 to maximize micropore area and overall micro plus mesopore area. There has been no effort in the prior art to make a support for bimetal catalyst application where the support has mesoporosity only.

The mesoporous supports disclosed in prior art have a large amount of micropores along with the mesopores.

SUMMARY

To help solve the problems of the prior art processes, one embodiment of the present invention is directed to a mesoporous carbon resin composition useful for producing an essentially mesoporous synthetic carbon; and a novel process for producing such essentially mesoporous synthetic carbon. It has been surprisingly found that by eliminating micropores from the carbon resin (e.g., by annealing synthetic carbon at extremely high temperature, i.e.
> 1000 °C) the uniformity of the bimetal alloy catalyst can be improved with the present invention.

In another embodiment, the present invention includes a mesoporous carbon support member made from the above mesoporous carbon resin composition.

In still another embodiment, the present invention includes a mesoporous catalyst product or article made using the above mesoporous carbon support member.

In yet other embodiments, the present invention includes processes for producing (i) the above mesoporous carbon resin composition, (ii) the above a mesoporous carbon support member, and (iii) the above mesoporous catalyst product or article.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic flow diagram of a process for making a mesopore carbon, a carbon support, and a catalyst of the present invention.

FIG. 2 is another schematic flow diagram of an alternative process for making a mesopore carbon, a carbon support, and a catalyst of the present invention.

FIG. 3 is a graphical illustration showing the atomic ratio of Pd/Ag nanometer particles on a catalyst.

DETAILED DESCRIPTION

Porous materials are typically classified into several kinds, categories, or types by the pore size of the porous material. In the present invention, a “mesoporous” material herein means a material containing pores with pore diameters between 2 nanometers (nm) and 100 nm; a “microporous” material herein means a material

containing pores with pore diameters of
< 2 nm; and a "macroporous" material herein means a material containing pores with pore diameters of greater than (>) 100 nm. Therefore, with regard to the pore diameter size category of the synthetic carbon mesoporous materials of the present invention, the average pore diameter size lies generally inbetween (i.e., the middle of) the diameter sizes of a microporous material and a macroporous material.

In the present invention, the final carbon support material can have porosities in the mesopore size and porosities in the micropore size; but the predominant size of the porosities is mesopores; and thus, the final carbon support material can be referred to herein as an "essentially mesoporous" carbon. And, an "essentially mesoporous" carbon herein means a carbon having a maximum number of porosities in the mesopore size (i.e., porosities predominantly in the mesopore size) and a minimum number of porosities in the micropore size (i.e., a carbon material substantially free of porosities in the micropore size). Thus, the "essentially mesoporous" synthetic carbon produced by the process of the present invention herein includes a synthetic carbon that has a combined volume of micropores (< 2 nm) and mesopores (from 2 nm to 50 nm); and the total area of micropores present in the synthetic carbon is generally < 50 percent (%) of the combined area of micropores and mesopores in the synthetic carbon in one embodiment, and < 30 % in another preferred embodiment.

"Pyrolysis" or "pyrolyzation", with reference to a thermal decomposition process to convert a polymeric resin into a carbonaceous material, herein means heating at a temperature of < 1,000 °C.

"Anneal" or "annealing", with reference to a high temperature process to collapse the micropores through carbon framework rearrangement, herein means heating at a temperature of higher than 1,000 °C.

A carbon formulation or composition (which is can also be referred to herein as a "carbon precursor composition") of the present invention, that can be used for preparing a carbon support structure, includes, for example, an admixture of: (a) a mesoporous carbon polymer resin precursor material having mesoporous particles; and (b) a macro-molecule carbon forming binder.

The mesoporous carbon polymer resin precursor that can be used to form: (1) a synthetic carbon; and (2) the mesopores in a final carbon support product, can be

derived from various carbon materials having mesoporous particles such as a cation exchange resin, a phenol formaldehyde resin, a polyacrylonitrile, a polyfurfural alcohol, and the like; and mixtures thereof. In a preferred embodiment, the mesoporous carbon polymer resin precursor can be selected from a cation exchange resin material, a phenol formaldehyde resin material, or a mixture thereof.

Exemplary of cation exchange resins useful as the mesoporous carbon polymer resin precursor can include AMBERLYST™ 15, AMBERLYST™ 35, DOWEX™ 88 all available from The Dow Chemical Company.

Exemplary of phenol formaldehyde resins useful as the mesoporous carbon polymer resin precursor can include AMBERLITE™ XAD761, commercially available from The Dow Chemical Company.

In general, the mesoporosity area of the mesoporous particles of component (a) used in the above carbon composition can be in the range of from 10 m^2/g to 500 m^2/g in one embodiment, from 20 m^2/g to 400 m^2/g in another embodiment, from 30 m^2/g to 300 m^2/g in still another embodiment, from 40 m^2/g to 300 m^2/g in yet another embodiment. and from
50 m^2/g to 200 m^2/g in even still another embodiment.

The beneficial properties of the mesoporous particles of component (a) can be achieved when the mesoporosity area of the mesoporous particles is predominantly of a mesoporous size. However, it is within the scope of the present invention for the mesoporous particles to include some amount of microporosity area in combination with the mesoporosity area. In a preferred embodiment, the microporosity area of the mesoporous particles can be minimized or eliminated as much as possible. For example, the microporosity area of the mesoporous particles of component (a) used in the above carbon composition can be in the range of less than 200 m^2/g in one embodiment, less than 100 m^2/g in another embodiment, and less than 50 m^2/g in still another embodiment.

The average mesopore diameter (i.e., the average diameter of the pores) of the mesoporous particles of the mesoporous polymer resin precursor, component (a), can be, for example, from 2 nm to 100 nm in one embodiment, from 3 nm to 80 nm in another embodiment, from 5 nm to 80 nm in still another embodiment, and from 10 nm to 50 nm in yet another embodiment.

The particle size of the mesoporous particles of component (a) can be an average particle size of from 0.1 micron (μm) to 1,000 μm in one embodiment, from 1 μm to 500 μm in another embodiment, and from 5 μm to 300 μm in still another embodiment.

Generally, the amount of the mesoporous carbon polymer resin precursor material, component (a), used in the formulation of the present invention can be generally for example from 30 weight percent (wt %) to 99 wt % in one embodiment, from 50 wt % to 97 wt % in another embodiment; and from 70 wt % to 95 wt % in still another embodiment; based on the total weight of all components in the formulation.

The macro-molecule carbon forming-binder material, component (b), of the present invention can include for example, a methylcellulose binder, coal tar pitch, phenolic resin, and mixtures thereof. In a preferred embodiment, the binder material can be a methylcellulose binder. For example, the methylcellulose binder useful in the carbon composition can include METHOCEL™ A4M, commercially available from The Dow Chemical Company.

In general, concentration of the binder material, component (b), used in the present invention may range generally from 1 wt % to 70 wt % in one embodiment, from 3 wt % to
50 wt % in another embodiment, and from 5 wt % to 30 wt % in still another embodiment, based on the total weight of all components in the formulation.

In one broad embodiment, the process for producing the carbon composition (which is also a precursor composition) of the present invention used for preparing a mesoporous carbon support structure as described above includes admixing: (α) a mesoporous material having mesoporous polymeric particles such as a cation exchange resin material (e.g., a sulfonated crosslinked polystyrene) or a phenol formaldehyde resin; and (β) a macro-molecule carbon forming binder such as a methylcellulose binder. Any other desired optional additives can be added to the above carbon composition.

In preparing the mesoporous carbon composition, the mixing of the components (α) and (β) can be carried out at a temperature of from -10 °C to 100 °C in one embodiment; from 0 °C to 80 °C in another embodiment; and from 10 °C to 50 °C in still another embodiment. The order of mixing of the ingredients is not critical and two

or more compounds can be mixed together followed by addition of the remaining ingredients. The ingredients that make up the carbon composition may be mixed together by any known mixing process and equipment.

With reference to FIG. 1, there is shown a schematic flow diagram of one embodiment of an overall process, generally indicated by numeral 10, for (i) making a mesopore carbon composition in the first steps shown in FIG. 1, followed by (ii) making a carbon support, and then (iii) making a catalyst article of the present invention. The steps of the process, as shown FIG. 1 include, but are not to be limited thereby, for example, providing a mesopore resin and binder mixture 11; pelletizing mesopore resin and binder mixture 11 in a pelletizing step 12 to form mesopore resin pellets 13; pyrolyzing the pellets 13 in a pyrolysis step 14 to form micro-mesopore carbon 15; annealing the micro-mesopore carbon 15 in a annealing step 16 to form a mesopore carbon 17; and impregnating a metal salt into the mesopore carbon 17 and calcining the metal salt impregnated mesopore carbon 17 in a metal salt impregnation/calcination step 18 to form a mesopore carbon catalyst 19.

With reference to FIG. 2, there is shown another schematic flow diagram of another embodiment of an overall process, generally indicated by numeral 20, for (i) making a carbon support in the first steps shown in FIG. 2, followed by (ii) making a mesopore carbon composition and then (iii) making a catalyst article of the present invention. The steps of the process, as shown FIG. 2 include, but are not to be limited thereby, for example, providing a mesopore resin 21; pyrolyzing the mesopore resin 21 in a pyrolysis step 22 to form a micro-mesopore carbon 23; annealing the micro-mesopore carbon 23 in a annealing step 24 to form a mesopore carbon 25; forming an admixture 26 of mesopore carbon and binder; pelletizing the mesopore carbon/binder mixture 26 in a pelletizing step 27 to form mesopore carbon/binder pellets 28; and impregnating a metal salt into the mesopore carbon/binder pellets 28 and calcining the metal salt impregnated mesopore carbon/binder pellets 28 in a metal salt impregnation/calcination step 29 to form a mesopore carbon catalyst 31. In an optional alternative embodiment, after the mesopore carbon/binder pellets 28 are formed in step 28, the mesopore carbon/binder pellets 28 can be further processed to carbonize the binder in the mesopore carbon/binder pellets 28 to form a mesopore carbon/carbonized binder pellets 32 and then the resulting pellets 32 can be impregnated with a metal salt

and the metal salt impregnated mesopore carbon/carbonized binder pellets 32 in a metal salt impregnation/calcination step 29 to form a mesopore carbon catalyst 31

The carbon formulation or composition of the present invention has advantageous properties and benefits. For example, the composition advantageously can be free of ash content and other impurities. By "free of ash content and other impurities", with reference to the carbon composition, it is meant that the content of ash and other impurities in the composition can be < 5 wt % in one embodiment, and < 0.5 wt % in another embodiment, based on the total weight of all the components in the carbon composition. The ash content and impurities content of the composition can be measured by the procedure described in ASTM D2866.

Another embodiment of the present invention is directed to a mesoporous carbon support structure made from the above carbon composition containing a majority of mesopores and a minority of micropores (a micro+mesoporous carbon composition). Generally, the mesoporous carbon support structure includes an annealed pyrolyzed carbon support structure resulting from annealing (e.g., > 1,000 °C) the above described micro+mesoporous carbon composition. The carbon support structure has a mesoporosity and a pore size which are derived from the mesoporosity and the pore size of the mesoporous carbon polymer resin precursor, component (a), of the above carbon composition.

In one general embodiment, the mesoporosity area of the carbon support structure can be in the range of from 10 m^2/g to 500 m^2/g, from 30 m^2/g to 400 m^2/g in another embodiment, and from 50 m^2/g to 300 m^2/g in still another embodiment; while the microporosity area of the carbon support structure can be in the range of less than 200 m^2/g in one embodiment, less than 100 m^2/g in another embodiment, and less than 50 m^2/g in still another embodiment. The mesopore size of the carbon support structure can be an average mesopore diameter size of from 2 nm to 100 nm in one embodiment, from 3 nm to 80 nm in another embodiment, and from
5 nm to 50 nm in still another embodiment.

In a broad embodiment of the present invention, the novel process for making the mesoporous carbon support structure includes the steps of pyrolyzing and annealing the unique mesoporous carbon formulation or composition described above. Pyrolysis, or inert thermal decomposition, can be used to convert the composition of the mesopore

carbon polymeric resin pellets into carbon structures. During this step, micropores are generated from the leaving of volatile gases. The macropores in the resin precursor are largely retained. Therefore, an essentially mesopore carbon which can contain micropores (a micro+mesopore carbon) is generated after an initial low temperature pyrolysis step.

With reference to FIG. 1 again, the process to make the mesoporous carbon support includes the steps from the palletization of the carbon composition (process flow step 12 in FIG. 1) to the annealing of micro-mesopore carbon (process flow step 16 in FIG. 1) to form the mesopore carbon support (shown in the flow diagram FIG. 1 as step 17).

For example, the novel carbon support structure (or formation) for accommodating a bi-metal or multi-metal catalyst system can be prepared by: (1) using mesoporous carbon material which provides the mesopores in the final carbon; and (2) using a high temperature (e.g., > 1,200 °C) annealing step so that any micropores generated from the decomposition/degassing of the carbon can be annealed away or reduced/minimized. The high temperature anneal step is very uncommon for typical known activated carbon processes because the heating of activated carbon is limited to a temperature of up to 1,000 °C whereas in the present invention a process with a high temperature annealing step can be used, viz, the annealing step 16 can be carried out a temperature of > 1,000 °C.

In one general embodiment, the process for making the unique mesoporous carbon support structure can include the steps of: (i) mixing the components (a) and (b) together to form a paste material; (ii) extruding the paste to form an extrudate (i.e. pellets); and then

(iii) pyrolyzing and simultaneously annealing the extrudate at a temperature of higher than, or equal to, 1,200 °C to create a micropore-free porous carbon structure, i.e., a mesoporous carbon support structure.

The pellets formed from the carbon composition of the present invention has advantageous properties and benefits. For example, the pellets advantageously can have a mechanical strength, as measured by the procedure described in ASTM D6175, of from

0.1 kg/mm to 10 kg/mm in one embodiment, from 0.5 kg/mm to 8 kg/mm in another embodiment, and from 1 kg/mm to 5 kg/mm in still another embodiment.

In carrying out the process of the present invention, extremely high temperature (e.g.,
> 1,200 °C) for a pyrolyzation and/or an annealing (heating) step of the process can be used to collapse most of the micropores present in a carbon material; and thus, the number of micropores in the carbon can be either eliminated or at least reduced to a minimum. It has been unexpectedly found that the collapse the micropores in the carbon enables the formation of compositional uniform nanoparticles catalytic metals such as for example Pd/Ag in the resulting mesopores of the carbon. Thus, the resulting mesoporous carbon, obtained using the high pyrolysis temperature, can be suitable for preparing a catalyst support that can, in turn, be used for preparing a multi-metal catalyst such as a highly selective Pd/Ag bimetal catalyst. The catalyst can then be used in a variety of chemical processes such as in acetylene selective hydrogenation, dichloroethane hydrodechlorination, hydrosilylation. The mesopore carbon structure enables the formation of compositional uniform nanoparticles such as a uniform Pd/Ag composition on all nanometer particles supported on the mesopore carbon structure. The mesopores are places where catalytic metal alloy nanometer particles exist for catalyst applications. The mesopore carbon of the present invention can also be useful to support other multi-metal catalysts for other reactions and applications. Thus, the bi-metal or multi-metal catalyst system of the present invention can be used in a broad range of applications.

In another specific embodiment, the process for producing a carbon support structure can include the steps of: (i) admixing: (α) a mesoporous material having mesoporous particles such as a mesoporous material derived from a cation exchange resin material or a phenol formaldehyde carbon material; and (β) a macro-molecule carbon forming binder such as a methylcellulose; (ii) mixing the mixture from step (i) with water to form an extrudable paste material; (iii) extruding the paste material from step (ii), via a die such as a 2 millimeters (mm) to 10 mm die, to form an extrudate; (iv) chopping or cutting the extrudate from step (iii) into shaped members such as from 2 mm to 10 mm length cylindrical-shaped members or from
2 mm to 10 mm spherical-shaped members (e.g., pellets); (v) drying and

simultaneously pyrolyzing the shaped members from step (iv) at a temperature of, for example, from 650 °C to 800 °C under an inert atmosphere such as nitrogen (N_2); and (vi) annealing the pyrolyzed chopped extruded paste material from step (v) at a temperature of at least equal to or higher than
1,200 °C under an inert atmosphere sufficient to create a micropore-free porous carbon support structure. In another embodiment, steps (v) and (vi) can be combined together in one step.

The pyrolyzing (heating) step of the process can be carried out at a temperature of from 400 °C to 1,000 °C in one embodiment; from 500 °C to 800 °C in another embodiment; and from 600 °C to 700 °C in still another embodiment. The amount time required for pyrolyzation may be for example from 0 minutes (min) to 1,000 min in one embodiment; from 10 min to
500 min in another embodiment; and from 30 min to 200 min in still another embodiment.

The annealing (heating) step of the process can be carried out at a temperature of from 1,000 °C to 2,500 °C in one embodiment; from 1,200 °C to 2,000 °C in another embodiment; and from 1,500 °C to 1,800 °C in still another embodiment. The amount time required annealing may be for example from 0 min to 1,000 min in one embodiment; from 10 min to
500 min in another embodiment; and from 30 min to 200 min in still another embodiment.

The carbon material used to form the carbon composition, i.e., the mesoporous polymer resin precursor material having mesoporous particles may include for example carbon particles, powder, beads, pellets, granules, aggregates, and the like. The carbon material can have various shapes such as spherical, tubular, rods, and the like. As aforementioned, when used in combination with a macro-molecule carbon forming binder, the carbon material can be formed, for example, in a paste for extruding in shaped members. The shaped members formed from the extrudate paste material can also be of any shape desired for the selected application. For example, the shape of the shaped members can include spherical, cylindrical, tubular, rods, elliptical, and the like; and mixtures thereof. In addition, the inert atmosphere used during the heating steps of

the process can be, for example, nitrogen, argon, and other inert gases; and mixtures thereof.

Any of the steps of the process of the present invention, such as extruding the paste material to form an extrudate; chopping or cutting the extrudate into shaped members; and heating the materials, can be carried out using any technique and ancillary equipment known in the art.

The mesoporous carbon support structure produced in accordance with the present invention advantageously has advantageous properties and benefits including, for example: (1) the carbon support can have a large surface area (e.g., > 30 m^2/g) of mesopores wherein the mesopores can be retained from the mesoporous polymer precursor; and (2) the carbon support can be essentially free of micropores wherein the micropores can be collapsed by high temperature (e.g., > 1,000 °C) annealing. The mesopore carbon support is also free of other impurities because the carbon support can be derived from synthetic resin and does not require any chemical activation.

The synthetic carbon of the present invention derived from a carbon material has several advantages compared to a carbon derived from known carbon materials using known processes. For example, the synthetic carbon: (1) has a higher activity; and (2) can be used in a simplified process to make the final synthetic carbon structure. In addition, a low temperature pyrolyzed carbon precursor, which is a low-cost starting material, can be annealed at a high temperature before the final bi-metal or multi-metal catalyst preparation step. The extremely high temperature (e.g., > 1,200 °C) annealing step and the carbon structure obtained using the high temperature annealing step can provide an effective catalyst while saving catalyst and process costs and while using a simplified process to make the effective catalyst. In addition, the extremely high temperature (e.g., > 1,200 °C) anneal step of the process can be beneficially used to remove the detrimental micropores from the carbon material; and to create a very pure carbon (C atomic composition higher than 95 weight percent (wt %) in one embodiment, and higher than 98 wt % in another preferred embodiment.

In one preferred embodiment, the carbon support structure of the present invention can be produced in the form of micropore-free carbon pellets that contain mesopores and a certain number of macropores (i.e., the carbon pellets are essentially

free of micropores). Advantageously, the carbon pellets also exhibit:(1) superior crush strength and (2) good interaction with metal nanoparticles.

An extrusion or pelletization process can be used to make beads or extrudate that have beneficial crush strength (e.g., > 0.1 kilograms per millimeter [kg/mm]), dimensions (e.g., 1 mm to 5 mm diameter and length), and porosities (e.g., 20 volume % [vol %] to 40 vol %). The crush strength of the pellets can be, for example, from 0.1 kg/mm to 10 kg/mm in one embodiment; from 0.5 kg/mm to 5 kg/mm in another embodiment; and from 1 kg/mm to 3 kg/mm in still another embodiment as measured by the process described in ASTM D6175.

The dispersion of composition of metal alloy nanoparticles on the carbon support can be measured by Transmission Electron Microscope (TEM). The average metal alloy particle can be for example, from 2 nm to 100 nm in one embodiment; from 3 nm to 80 nm in another embodiment; and from 5 nm to 50 nm in still another embodiment as measured by TEM.

As an illustration of one embodiment of the present invention, the carbon pellets can include a carbon support structure including: (a) mesoporous particles with a mesopore area in the range of from 10 m^2/g to 500 m^2/g, an average mesopore diameter of from 2 nm to 100 nm, and an average particle size of from 0.1 μm to 100 μm.

It has been surprisingly and unexpectedly found that, by using mesopore carbon materials which have been annealed at a high temperature of above 1,200 °C to form a bi-metal or multi-metal catalyst support, a bi-metal or multi-metal catalyst containing metal alloy particles of uniform composition can be obtained. In addition, the bi-metal or multi-metal catalyst can catalyze the desired reaction very selectively.

The multi-metallic catalyst of the present invention includes a combination of: (A) an annealed pyrolyzed mesopore carbon structure having a mesoporosity of >20 m^2/g and an average mesopore diameter of from 2 nm to 50 nm; and (B) at least two or more metallic particles disposed throughout the mesoporosity of the annealed pyrolyzed mesopore carbon structure. As described above, to produce the multi-metallic catalyst, the annealed pyrolyzed carbon, component (A), can be prepared from a mesoporous material having mesoporous particles derived from a cation exchange resin material or a phenol formaldehyde polymeric precursor. Exemplary of the two metallic particles, component (B) in the above multi-metallic catalyst, can include, first

metallic particles of palladium and second metallic particles of silver (e.g., a Pd/Ag catalyst). Other metallic particles for the catalyst can include platinum (Pt), copper (Cu), and mixtures thereof.

In a broad embodiment, the catalyst of the present invention can be manufactured by disposing at least two metals in the catalyst support member described above. In a preferred embodiment, the process for producing the multi-metallic catalyst of the present invention can include the steps of: (I) providing an annealed pyrolyzed carbon structure having a mesoporosity of > 20 m^2/g and an average mesopore diameter of 2 nm to 50 nm; and (II) impregnating the annealed pyrolyzed carbon structure of step (I) with at least two or more catalytic metallic particles throughout the mesoporosity of the annealed pyrolyzed carbon structure such that at least a portion of the two or more catalytic metallic particles are deposited throughout the mesoporosity of the annealed pyrolyzed carbon structure. As aforementioned, the annealed pyrolyzed carbon structure can be obtained from a mesoporous material having mesoporous particles derived from a cation exchange resin material or a phenol formaldehyde carbon material; and the two metallic particles can include first metallic particles of palladium and second metallic particles of silver.

The catalyst made in accordance with the present invention can be useful in a variety of applications including, for example, selective hydrogenation, hydrodechlorination, hydroformylation, hydrosilylation, and the like.

EXAMPLES

The following examples are presented to further illustrate the present invention in detail but are not to be construed as limiting the scope of the claims. Unless otherwise stated all parts and percentages are by weight.

Various raw materials used in the Inventive Examples (Inv. Ex.) and the Comparative Examples (Comp. Ex.) herein are described in Table I as follows:

Table I – Raw Materials

Component	Brief Description	Supplier
AMBERLYST™ 15DRY	Mesoporous cation exchange resin	The Dow Chemical Company
AMBERLYST™ 35DRY	Mesoporous cation exchange resin	The Dow Chemical Company
AMBERLITE™ XAD761DRY	Mesoporous phenol formaldehyde resin	The Dow Chemical Company

METHOCEL™ A4M	Binder	The Dow Chemical Company

Examples 1 – 5 and Comparative Examples A and B

In these Examples, two different mesoporous cation exchange resin products, AMBERLYST™ 15 and AMBERLYST™ 35, were used to prepare a carbon composition, which in turn, was used for preparing a catalyst support structure. The catalyst support structure was then, in turn, used for preparing a catalyst. The catalysts used in the Examples and the catalyst performance results are described in Table II. The various general procedures used for preparing and testing the catalysts of the Examples are also described herein below.

Table II – Catalyst Preparation and Performance Results

Example	Carbon Form	Precursor	Final Pyrolysis/ Annealing Temperature (^{0}C)	Average Pore Radius - BJH Adsorption (nm)	Micropore Area (m^2/g)	Mesopore Area (m^2/g)
Comp. Ex. A	Powder	AMBERLYST™ 15	850	8.7	423	31
Inv. Ex. 1	Powder	AMBERLYST™ 15	1300	13.3	20	40
Inv. Ex. 2	Powder	AMBERLYST™ 15	1500	12.6	10	37
Inv. Ex. 3	Powder	AMBERLYST™ 15	1700	11.2	8	35
Comp. Ex. B	Powder	AMBERLYST™ 35	850	9.9	492	51
Inv. Ex. 4	Powder	AMBERLYST™ 35	1700	11.7	30	55
Inv. Ex. 5	Pellet	AMBERLYST™ 15	1700	10.9	6	28

General Procedure for Pelletization

A wet cation exchange resin, AMBERLYST™ 15 or AMBERLYST™ 35, with a resin bead (~500 microns in diameter) was milled into powder using an Alpine mill. The milled powder has a D50 (volume cumulative 50 % point of diameter) of 22 μm, as measured by laser diffraction method in dry powder form. A binder, METHOCEL™ A4M, and the milled cation exchange resin were mixed together using an automatic low-shear kitchen mixer. The weight ratio of the binder/dry resin was kept at 3/100. Water was gradually added to the binder/dry resin mixture until a paste formed with a good balance of viscosity and stickiness such that the mixture had a consistent rheology to be extrudable. A 5 centimeter (cm)-diameter ram extruder with a maximum working

cylinder pressure of 200 Bar was used for extruding the paste material. The paste was loaded into the barrel of the ram extruder and the ram was advanced at various rates (e.g., 0.25 centimeters per minute (cm/min) to 1 cm/min) to force the paste through a shaping die. The paste was extruded through a 4 mm internal diameter (ID) die and automatically cut into cylindrical pellets of approximately 4-10 mm in length. The pellets were dried in an air purged oven at 50 ^{0}C overnight.

General Procedure of Pyrolysis

Approximately 60 grams (g) of dried powder or pellets was loaded into a 6-inch (15.2 cm) quartz tube furnace purged with nitrogen at a rate of 2 liters per minute (L/min). A scrubber connected to the furnace contained a 10 wt % sodium hydroxide aqueous solution. The loaded tube furnace was heated to a final temperature of either 300 °C or 850 °C at a rate of 5 degrees Celsius per minute (°C/min) and then the temperature of the furnace was held for
30 min before cooling the furnace to ambient temperature (about 25 °C).

General Procedure for Annealing

Approximately 60 g of dried pellets, of the carbons pyrolyzed at 1700 °C, was pre-pyrolyzed in a 6-inch (15.2 cm) quartz tube furnace to 850 °C at 5 °C/min and held for
30 min. A subsequent higher temperature pyrolysis was then carried out in a graphite furnace. About 20 g of the pre-pyrolyzed carbon obtained from the quartz tube furnace was loaded into a graphite boat having the dimensions of 4 inches x 4 inches x 0.5 inch (10.2 cm x 10.2 cm x
1.3 cm). The boat containing the pre-pyrolyzed carbon sample was heated to 1700 °C at
10 °C/min and held for 30 min, with a nitrogen purge at 10 L/min (one volume turnover in every 12 min). After pyrolysis of carbon sample, the graphite furnace was cooled at 10 °C/min to 450 °C, below which the furnace was allowed to cool to ambient temperature at a slower rate due to heat transfer limitations.

General Procedure for Catalyst Impregnation

Approximately 0.449 g $AgNO_3$ salt (99.9999 % purity, available from Premion) and 1.556 g of $Pd(NO_3)_2$ salt in excess nitric acid solution (13.82 wt % Pd metal, available from Heraeus) were added into a 50 milliliters (mL) jar. Additional deionized

water (impregnation volume from BET minus 1.556 g of $Pd(NO_3)_2$ salt solution) was added into the jar and hand-shaken to form a homogeneous solution. Approximately 10 g of carbon was added into the jar and the resulting solution/carbon mixture was hand-shaken in the jar closed to the atmosphere. Then, the jar was opened and the contents of the jar exposed to air such that the solution/carbon mixture in the jar dried overnight at room temperature. After the mixture dried overnight, the resulting impregnated catalyst was then dried at 120 °C with a 1 °C/min ramp for 12 hours (hr) under air purge. The dried impregnated catalyst was then placed into a 6-inch (15.2 cm) diameter quartz tube furnace and heated to 500 °C at 5 °C/min and held for 30 min. Then, the quartz tube furnace was cooled to ambient temperature.

All of the catalysts described in Table II had the same metal loading: 2.15 wt % Pd and 2.85 wt % Ag. The impregnated catalysts were then further calcined at 500 °C. The catalysts of Comp. Ex. A and Comp. Ex. B had the largest amount of micropores compared to the Inv. Ex. 1-5.

Examples 6 – 8 and Comparative Example C

In these Examples, a phenol formaldehyde resin (AMBERLITE™ XAD761) was used as the mesoporous polymer resin. The mesoporous material was used to prepare a carbon composition, which in turn, was used for preparing a catalyst support structure. The catalyst support structure was then, in turn, used for preparing a catalyst. The catalysts used in the Examples and the catalyst performance results are described in Table III. The various general procedures used for preparing and testing the catalysts of the Examples are described herein below.

Table III – Catalyst Preparation and Performance Results

Example	Carbon Form	Precursor	Final Pyrolysis/Annealing Temp. (^{0}C)	Average pore radius-BJH Adsorption (nm)	Micropore Area (m^2/g)	Mesopore Area (m^2/g)	Average Pd/Ag ratio [-]
Comp. Ex. C	Powder	AMBERLITE ™ XAD761	850	3.8	473	176	1.07
Inv. Ex. 6	Powder	AMBERLITE ™ XAD761	1300	4.0	156	183	0.43
Inv. Ex. 7	Powder	AMBERLITE ™ XAD761	1500	4.4	139	139	0.38
Inv. Ex. 8	Powder	AMBERLITE ™ XAD761	1700	4.3	68	120	0.43

General Procedure of Pyrolysis

Approximately 60 g of dried resin powder was loaded into a 6-inch (15.2 cm) quartz tube furnace purged with nitrogen at a rate of 4-4.5 L/min. A scrubber connected to the furnace contained a 10 wt % sodium hydroxide aqueous solution. The loaded quartz tube furnace was heated to a final temperature of 850 °C at a rate of 5 °C/min; and then, the temperature of the furnace was held for 30 min before cooling the furnace to ambient temperature.

General Procedure for Annealing

Approximately 20 g of pre-pyrolyzed carbon (which was pyrolyzed at 850 °C at 5 °C/min and held for 30 min in the 6-inch (15.2 cm) quartz tube furnace described above in the pyrolysis procedure) was subsequently pyrolyzed at higher temperature in a graphite furnace. About 20 g of the pre-pyrolyzed carbon obtained from the quartz tube furnace was loaded into the graphite boat having the dimensions of 4 inches x 4 inches x 0.5 inch (10.2 cm x 10.2 cm x 1.3 cm). The graphite boat containing the pre-pyrolyzed carbon sample was then heated to a final temperature of 1,300 °C, 1,500 °C, and 1,700 °C at 10 °C/min and held for 30 min, with a nitrogen purge at 10 L/min (one volume turnover in every 12 min). After pyrolysis of the carbon sample, the furnace was cooled at 10 °C/min to 450 °C, below which the furnace was allowed to cool to ambient temperature at a slower rate due to heat transfer limitations.

General Procedure for Catalyst Impregnation

Approximately 0.898 g $AgNO_3$ salt (99.9999 percent (%) purity, available from Premion) and 1.556 g of $Pd(NO_3)_2$ salt in excess nitric acid solution (13.82 wt % Pd metal, available from Heraeus) were added into a 50 mL jar. Additional deionized water (impregnation volume from BET minus 1.556 g of $Pd(NO_3)_2$ salt solution) was added into the jar and hand-shaken to form a homogeneous solution. Approximately 10 g of carbon was added into the jar and the resulting solution/carbon mixture was hand-shaken in the jar closed to the atmosphere. Then, the jar was opened and the contents of the jar exposed to air such that the solution/carbon mixture in the jar dried overnight at room temperature. After the mixture dried overnight, the resulting impregnated catalyst was then dried at 120 °C with a 1 °C/min ramp for 12 hr under air purge. The dried impregnated catalyst was then placed into a 6-inch (15.2 cm) diameter quartz tube

furnace and heated to 500 °C at 5 °C/min and held for 30 min. Then, the quartz tube furnace was cooled to ambient temperature.

All of the catalysts described in Table II had the same metal loading: 2.15 wt % Pd and 5.70 wt % Ag. The impregnated catalyst was then were further calcined at 500 °C.

Carbon Catalyst

Pd/Ag nanoparticles were imaged using Scanning Transmission Electron Microscopy - High Angle Annular Dark Field (STEM-HAADF); the composition of the Pd/Ag nanoparticles was determined using x-ray energy-dispersive spectroscopy (XEDS). Two to five hundred individual particle sizes and composition were measured using a custom Python script. As shown in FIG. 2 and Table III above, the compositional distribution of the nanometer metal alloy particles changes significantly on different carbon support. The catalyst of Comp. Ex. C has the widest distribution of Pd/Ag ratios and may have less selectivity in catalytic systems. The catalyst of Comp. Ex. C has the largest amount of micropores, which probably caused the separation of the larger Pd2+ hydrated ion and the smaller Ag+ hydrated ion during the wet impregnation stage. Annealing the carbon at a temperature above 1,200 °C reduces the amount of micropores. The catalysts of Inv. Ex. 6, 7, and 8 have nanometer alloy particles of much more uniform compositions. The catalyst of Inv. Ex. 6, 7, and 8 having a higher compositional uniformity can advantageously catalyze reactions more selectively.

Exemplary embodiments include the following:

(1) A carbon composition used for preparing a catalyst support structure including an admixture of: (a) a mesoporous material having mesoporous particles; and (b) a macro-molecule carbon forming binder.

(2) The carbon composition of embodiment (1) above, wherein the mesoporous material having mesoporous particles is derived from a cation exchange resin material or a phenol formaldehyde carbon material.

(3) The carbon composition of embodiment (1) above, wherein the mesoporosity area of the mesoporous particles of component (a) is in the range of from 10 m^2/g to 500 m^2/g; wherein the average mesopore diameter of the mesoporous

particles is from 2 nanometers to 100 nanometers; and wherein the particle size of the mesoporous particles is an average particle size of from 0.1 micron to 100 microns.

(4) The carbon composition of embodiment (1) above, wherein the macro-molecule carbon forming binder is methylcellulose.

(5) A process for producing a carbon composition used for preparing a catalyst support structure including admixing: (α) a mesoporous material having mesoporous particles; and (β) a macro-molecule carbon forming binder.

(6) The process of embodiment (5) above, wherein the mesoporous material having mesoporous particles is derived from a cation exchange resin material or a phenol formaldehyde carbon material.

(7) The process of embodiment (5) above, wherein the macro-molecule carbon forming binder is methylcellulose.

(8) A carbon support structure including an annealed pyrolyzed carbon structure having a mesoporosity area of from 10 m^2/g to 500 m^2/g and an average mesopore diameter of from 2 nanometers to 50 nanometers.

(9) A process for producing a carbon support structure including the steps of:

(i) admixing: (α) a mesoporous material having mesoporous particles; and (β) a macro-molecule carbon forming binder;

(ii) mixing the mixture from step (i) with water to form an extrudable paste material;

(iii) extruding the paste material from step (ii), via a 2 millimeters to 10 millimeters die;

(iv) chopping the extruded paste material from step (iii) into 2 millimeters to 10 millimeters length cylinders;

(v) drying and simultaneously pyrolyzing the chopped extruded paste material from step (iv) at a temperature of 650 °C to 800 °C under an inert atmosphere; and

(vi) annealing the pyrolyzed chopped extruded paste material from step (v) at a temperature of at least 1,200 ^0C under an inert atmosphere.

(10) The process of embodiment (9) above, wherein the mesoporous material having mesoporous particles is derived from a cation exchange resin material or a phenol formaldehyde carbon material.

(11) The process of embodiment (9) above, wherein the macro-molecule carbon forming binder is methylcellulose.

(12) A multi-metallic catalyst including: (A) an annealed pyrolyzed carbon structure having a mesoporosity of from 10 m^2/g to 500 m^2/g and an average mesopore diameter of from 2 nanometers to 50 nanometers; and (B) at least two or more metallic particles disposed throughout the mesoporosity of the annealed pyrolyzed carbon structure.

(13) The multi-metallic catalyst of embodiment (12) above, wherein the annealed pyrolyzed carbon is obtained from a mesoporous material having mesoporous particles derived from a cation exchange resin material or a phenol formaldehyde carbon material.

(14) The multi-metallic catalyst of embodiment (12) above, wherein the annealed pyrolyzed carbon includes a macro-molecule carbon forming binder is methylcellulose.

(15) The multi-metallic catalyst of embodiment (12) above, wherein the two metallic particles include first metallic particles of palladium and second metallic particles of silver.

(16) A process for producing a multi-metallic catalyst including the steps of:

(I) providing an annealed pyrolyzed carbon structure having a mesoporosity of from
10 m^2/g to 500 m^2/g and a mesopore size of from 2 nanometers to 50 nanometers; and

(II) impregnating the annealed pyrolyzed carbon structure of step (I) with at least two or more catalytic metallic particles throughout the mesoporosity of the annealed pyrolyzed carbon structure such that at least a portion of the two or more catalytic metallic particles are deposited throughout the mesoporosity of the annealed pyrolyzed carbon structure.

(17) The process of embodiment (16) above, wherein the annealed pyrolyzed carbon structure is obtained from a mesoporous material having mesoporous particles derived from a cation exchange resin material or a phenol formaldehyde carbon material.

(18) The process of embodiment (16) above, wherein the annealed pyrolyzed carbon structure includes a macro-molecule carbon forming binder is methylcellulose.

(19) The process of embodiment (16) above, wherein the two metallic particles include first metallic particles of palladium and second metallic particles of silver.

WHAT IS CLAIMED IS:

1. A catalyst support structure, comprising:

a carbon composition that includes an admixture of (a) a mesoporous material having mesoporous particles; and (b) a macro-molecule carbon forming binder.

2. The catalyst support structure as claimed in claim 1, wherein the mesoporous material having mesoporous particles is derived from a cation exchange resin material or a phenol formaldehyde carbon material.

3. The catalyst support structure as claimed in claim 1 or claim 2, wherein:

the mesoporosity area of the mesoporous particles of component (a) is in the range of from 10 m^2/g to 500 m^2/g; the microporosity area of the mesoporous particles of component (a) is in the range of less than 200 m^2/g; the average mesopore diameter of the mesoporous particles is from 2 nanometers to 100 nanometers; and the particle size of the mesoporous particles is an average particle size of from 0.1 micron to 100 microns.

4. The catalyst support structure as claimed in any one of claims 1 to 3, wherein the macro-molecule carbon forming binder is methylcellulose.

5. A catalyst support structure as claimed in any one of claims 1 to 4, wherein the catalyst support structure includes an annealed pyrolyzed carbon structure.

6. The catalyst support structure as claimed in claim 5, further comprising at least two or more metallic particles disposed throughout the mesoporosity area of the annealed pyrolyzed carbon structure to form a multi-metallic catalyst.

7. The catalyst support structure as claimed in claim 6, wherein the two metallic particles include first metallic particles of palladium and second metallic particles of silver.

8. A process for producing the catalyst support structure as claimed in any one of claims 1 to 7, the process comprising the steps of:

(i) admixing the (a) mesoporous material having mesoporous particles; and (b) the
macro-molecule carbon forming binder;

(ii) mixing the mixture from step (i) with water to form an extrudable paste material;

(iii) extruding the paste material from step (ii), via a 2 millimeters to 10 millimeters die;

(iv) chopping the extruded paste material from step (iii) into 2 millimeters to 10 millimeters length cylinders;

(v) drying and simultaneously pyrolyzing the chopped extruded paste material from step (iv) at a temperature of 650 °C to 800 °C under an inert atmosphere; and

(vi) annealing the pyrolyzed chopped extruded paste material from step (v) at a temperature of at least 1,200 °C under an inert atmosphere.

FIG. 1A

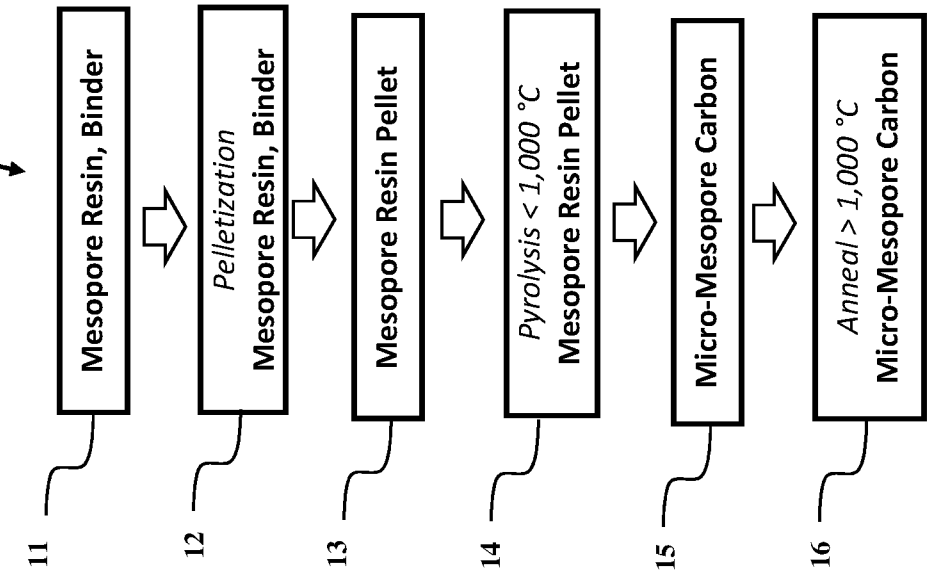
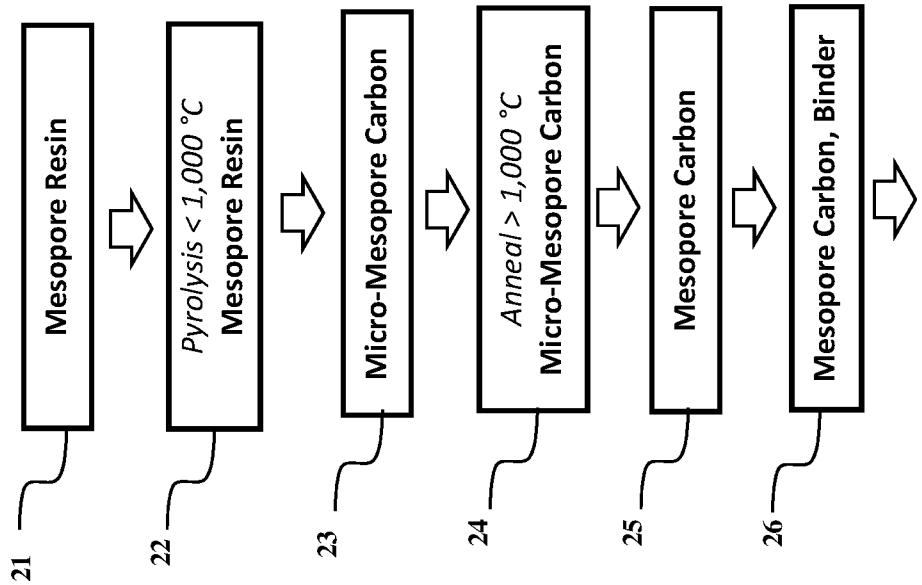

10
Mesopore Resin, Binder
Pelletization
Mesopore Resin, Binder
Mesopore Resin Pellet
Pyrolysis < 1,000 °C
Mesopore Resin Pellet
Micro-Mesopore Carbon
Anneal > 1,000 °C
Micro-Mesopore Carbon
11
12
13
14
15
16

FIG. 2A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Mesopore Resin
Pyrolysis < 1,000 °C
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Micro-Mesopore Carbon
Anneal > 1,000 °C
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Mesopore Carbon
Mesopore Carbon, Binder
21
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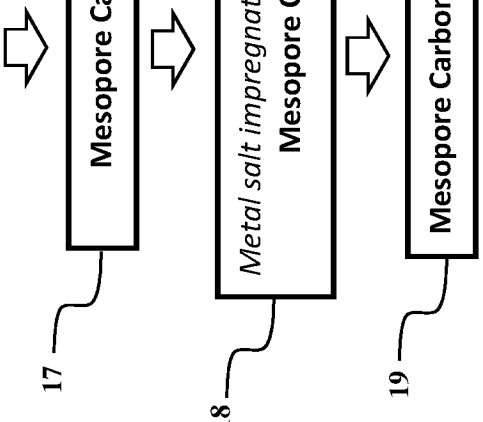
26

FIG. 1B


Mesopore Carbon
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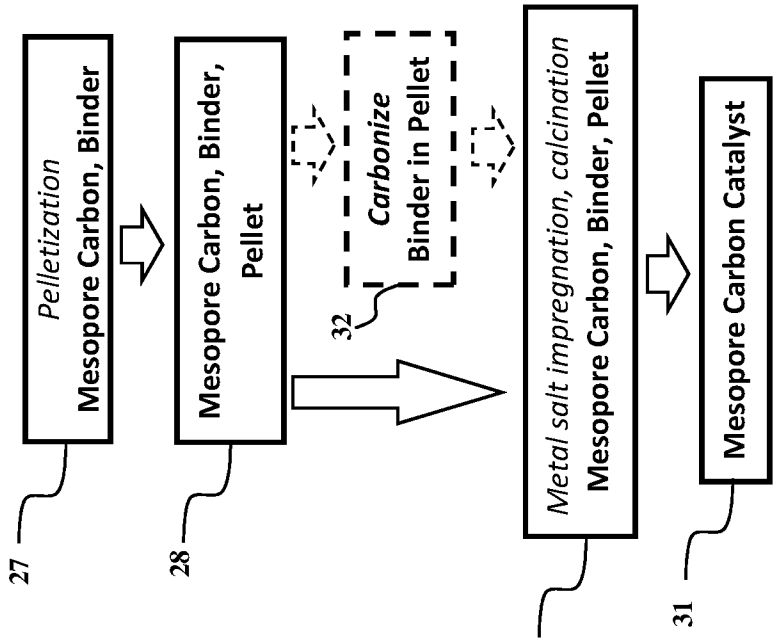
Metal salt impregnation, calcination
Mesopore Carbon
18
Mesopore Carbon Catalyst
19

FIG. 2B


Pelletization
Mesopore Carbon, Binder
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Mesopore Carbon, Binder, Pellet
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Carbonize
Binder in Pellet
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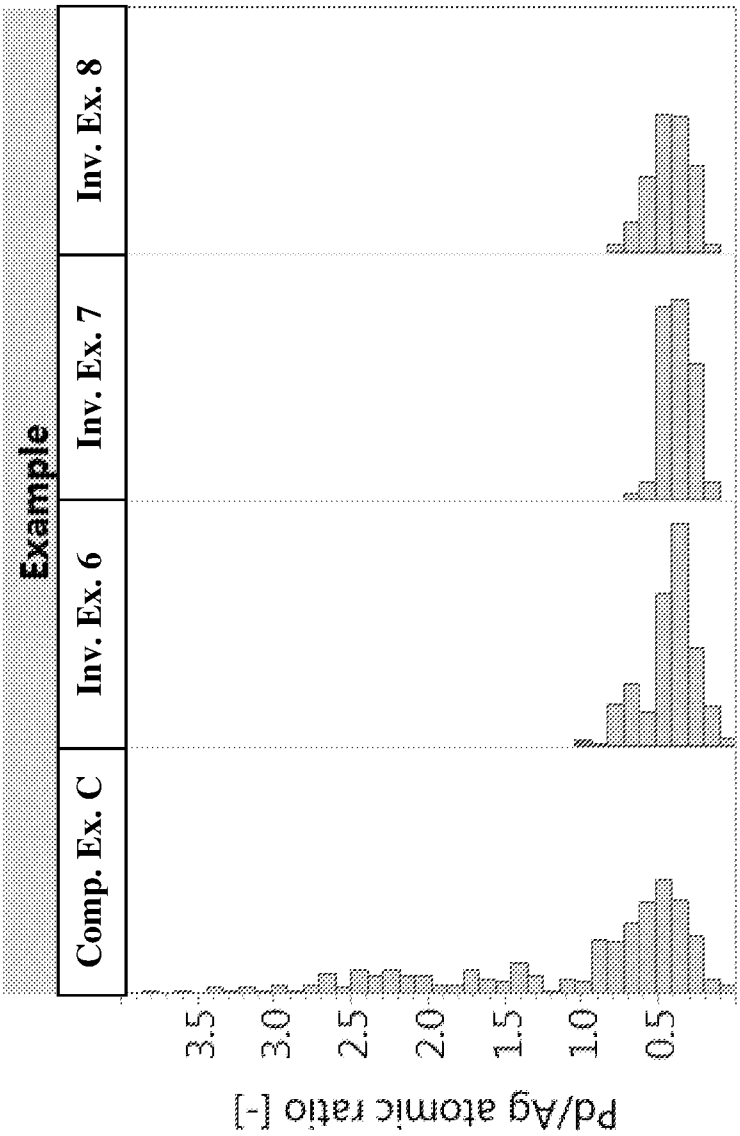
Metal salt impregnation, calcination
Mesopore Carbon, Binder, Pellet
29
Mesopore Carbon Catalyst
31

FIG. 3


Example
Comp. Ex. C
Inv. Ex. 6
Inv. Ex. 7
Inv. Ex. 8
Pd/Ag atomic ratio [-]
3.5
3.0
2.5
2.0
1.5
1.0
0.5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/060041

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J37/08 B01J37/00 B01J21/18 B01J23/50 B01J35/02
B01J35/10 B01J37/02 B01J35/00 C01B32/30 C01B32/312
C01B32/318

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07C C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/009662 A1 (C-TEX LTD [GB]; UNIV OF BRIGHTON [GB]) 19 January 2017 (2017-01-19)	1-6
Y	abstract page 5, lines 6-26 page 6, lines 1-2, 19-32 page 7, lines 1, 6-9, 23-32 page 8, lines 1-4, 27-28 page 12, lines 7-10 page 16, lines 9-14, 21 page 28, lines 10-20 example 4	8

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 March 2020	07/04/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schön, Anke

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/207096 A1 (SICAT [FR]; SASOL TECH PTY LTD [ZA]) 31 December 2014 (2014-12-31)	1-6
Y	page 5, lines 15-21, 29-35 page 6, lines 1-4 pages 7-8, lines 35-1, 14-15 pages 10-11, lines 36-2, 20-23 page 15, lines 1-15, 21-28 page 16, lines 31-38 page 18, lines 6-11, 22-24 page 19, lines 25-38 page 20, lines 11-12; claims 1-4; figures 6, 10; examples 4, 5, 7; table 1	8

X	YINGYING LV ET AL: "A comprehensive study on KOH activation of ordered mesoporous carbons and their supercapacitor application", JOURNAL OF MATERIALS CHEMISTRY, vol. 22, no. 1, 11 October 2011 (2011-10-11), pages 93-99, XP055679108, GB ISSN: 0959-9428, DOI: 10.1039/C1JM12742J	1-3,5
A	"2.2 Synthesis of ordered mesoporous carbon", "4. Conclusion"; figure 3; examples FDU-15; table 1	4,6-8

X	US 4 439 349 A (EVERETT DOUGLAS H [GB] ET AL) 27 March 1984 (1984-03-27)	1-8
Y	column 1, lines 1-8, 40-60 column 4, lines 49-51, 61-68 column 5, lines 1-6 column 7, lines 13-29; figure 1; examples	8

A	VERMA PRIYANKA ET AL: "Mesoporous silica supported Pd/Ag bimetallic nanoparticles as a plasmonic catalyst for chemoselective hydrogenation of p-nitrostyrene under visible light irradiation", JOURNAL OF CHEMICAL SCIENCES, SPRINGER INDIA, IN CO-PUBLICATION WITH INDIAN ACADEMY OF SCIENCES, INDIA, vol. 129, no. 11, 19 September 2017 (2017-09-19), pages 1661-1669, XP036378210, ISSN: 0974-3626, DOI: 10.1007/S12039-017-1364-5 [retrieved on 2017-09-19] abstract	1-8

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2019/060041

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017009662 A1	19-01-2017	EP 3322518 A1	23-05-2018
		US 2019022623 A1	24-01-2019
		WO 2017009662 A1	19-01-2017
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