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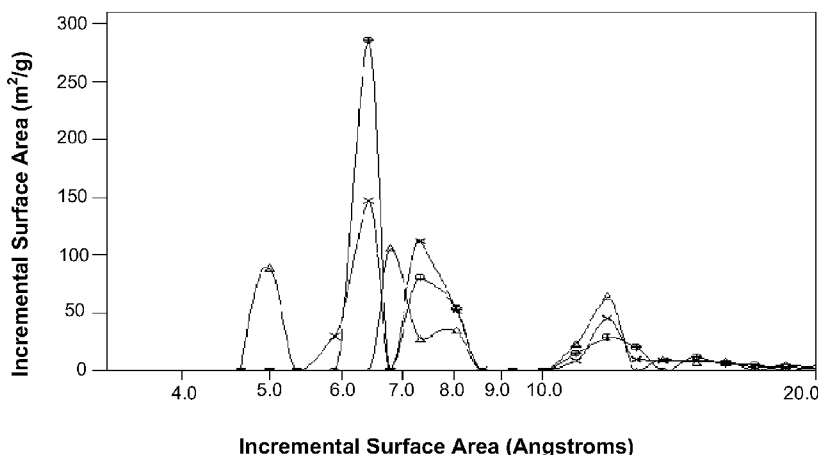


FIG. 1

(57) Abstract: A carbon molecular sieve composition for storing hydrogen and a method for forming a carbon molecular sieve material is provided. In addition, a method of storing hydrogen using the carbon molecular sieve composition and a method for separating gases such as hydrogen or helium from mixtures of other gases is provided.

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## **CARBON MOLECULAR SIEVE FOR HYDROGEN STORAGE AND ADSORPTION OF OTHER LIGHT GASES**

### **FIELD OF THE INVENTION**

[0001] The present invention relates to methods of forming a carbon molecular sieve and the use of the carbon molecular sieve for the adsorption of hydrogen and other light gases. Further, the invention relates to the use of the carbon molecular sieve for hydrogen storage and/or for the separation of gases such as hydrogen and helium from mixtures of other gases.

### **BACKGROUND OF THE INVENTION**

[0002] Hydrogen has emerged as a promising clean energy source, particularly in transportation applications. Current hydrogen fuel cells used to power automobiles are as much as 2-3 times more efficient than internal combustion engines that are powered by conventional hydrocarbon fuels. Although molecular hydrogen has a high energy density by weight, hydrogen has very low energy density by volume at ambient temperature and pressure. In order to store a usable amount of hydrogen fuel compactly, the hydrogen fuel may be stored cryogenically, compressed, or bound reversibly to various chemical compounds and surfaces.

[0003] The hydrogen may be cryogenically treated and stored as relatively dense liquid hydrogen. However, the cryogenic equipment necessary to freeze and maintain the hydrogen in a liquid state consumes energy and adds extra weight, reducing the energy efficiency and cost effectiveness of any system utilizing liquid hydrogen. The extremely low temperatures of the liquid hydrogen pose a challenge in designing the structure of the fuel tank and surrounding structures that must function at ambient temperatures. In addition, liquid hydrogen is a hazardous substance to handle, making the widespread use of liquid hydrogen difficult to implement.

[0004] Compressed hydrogen requires additional compressors that add weight and consume energy. In addition, the pressurized fuel tank requires additional strengthening material to prevent a potentially dangerous rupture, adding further weight.

[0005] Chemical compounds, such as metal hydrides, may be used as a reversible storage medium for hydrogen. Metal hydrides may be produced in the

form of easily handled liquids, or solid membranes or pellets at ambient temperature and pressure. Although metal hydrides have good energy density by volume, their energy density by weight is often considerably lower than hydrocarbon fuels, and high temperatures are often required to release their hydrogen content. In addition, some metal hydrides are toxic to humans when in contact with the skin or eyes, and may combust violently when exposed to moist air. Further, the efficiency of metal hydrides and other chemical compounds is sensitive to contaminants in the hydrogen fuel that may alter the chemical surface of the compounds.

[0006] Hydrogen fuel may also be stored in synthetic porous materials such as metal-organic frameworks in the form of solid membranes or pellets. Metal-organic porous frameworks store hydrogen by adsorption within the pores of the material. Synthetic porous pellets may be scooped or poured relatively easily, and are capable of adsorbing and storing hydrogen at near-ambient conditions. However, existing synthetic porous materials may require extremely low operating temperatures to achieve sufficiently high storage densities. Further, in order to store hydrogen at optimal efficiency at temperatures and pressures near ambient conditions, the pores of the material must fall within a narrow size range matched to the size of the hydrogen molecules to be stored.

[0007] Synthetic porous materials such as zeolite and activated charcoal have been also been used to adsorb compounds from gas and liquid streams in diverse applications such as desulfonation of refinery feed streams, chromatography, and waste water filtration. Many of these applications use synthetic porous materials with a predetermined distribution of pore sizes, or various alterations of the surface chemistry of the material to achieve the desired specificity of the porous material for the adsorbate to be captured.

[0008] Small airborne molecules such as hydrogen, methane, or krypton may be captured using synthetic nanoporous materials with pore sizes of less than about 10 angstroms as well. For a synthetic porous material to adsorb a particular airborne compound to the exclusion of other compounds, the pores of the materials must fall within a relatively narrow range of sizes. Existing methods of fabricating synthetic porous materials lack the ability to control the range of ultramicropore sizes to within the necessary range of variation.

[0009] A need exists for a hydrogen storage material that is capable of reversibly storing and releasing hydrogen at near-ambient conditions, is relatively non-toxic, is relatively easy to handle and store, does not require excessive additional equipment to store and release hydrogen, and is relatively insensitive to the presence of contaminants in the hydrogen to be stored. In particular, a need exists for a solid synthetic porous material that reversibly captures hydrogen and other small airborne compounds at near-ambient temperature and pressure conditions. Such a material may also be used for the purification of helium, a gas that is in relatively short supply, by separating the desired helium from hydrogen, argon, neon, and other small molecular gases.

### **SUMMARY OF THE INVENTION**

[0010] The present invention provides a carbon molecular sieve (CMS), methods of producing the CMS, methods of using the CMS for the storage of hydrogen or other small-molecule gases, and methods of using the CMS to separate a small-molecule gas from a mixture of gases that includes the small-molecule gas.

[0011] In one embodiment, the CMS includes an amount of carbon equal to or greater than about 99% by weight of the CMS. The CMS also includes a plurality of micropore sidewalls forming interconnected micropores with internal diameters ranging from about 10 Å to about 20 Å; the micropore sidewalls comprise from about 5% to about 40% of the total surface area of the CMS. In addition, the CMS includes a plurality of ultramicropore sidewalls forming interconnected ultramicropores with mean internal diameters ranging from about 3.0 Å to about 10 Å and individual internal diameters within about 0.5 Å of the mean internal diameter; the ultramicropore sidewalls comprise from about 10% to about 60% of the total surface area of the CMS.

[0012] In another embodiment, the CMS is an essentially spherical particle containing an amount of carbon equal to or greater than about 99% by weight of the CMS. The diameters of the CMS particles range from about 2 μm to about 1000 μm. Each spherical CMS particle contains a plurality of micropore sidewalls forming interconnected micropores having internal diameters ranging from about 10 Å to about 20 Å; the micropore sidewalls comprise from about 5% to about 40% of the total surface area of the CMS particle. In addition, the spherical CMS

particle also includes a plurality of ultramicropore sidewalls forming ultramicropores having a mean internal diameter ranging from about 3 Å to about 7 Å, and individual internal diameters within about 0.5 Å of the mean internal diameter; the ultramicropore sidewalls comprise from about 10% to about 60% of the total surface area of the CMS particles.

[0013] In an additional embodiment, a method for forming a carbonaceous adsorbent is provided that includes polysulfonating a microporous polymer ion exchange resin to produce a polysulfonated ion exchange resin, and pyrolyzing the polysulfonated ion exchange resin to produce the carbonaceous adsorbent.

[0014] Another additional embodiment provides a method of forming a carbon molecular sieve that includes polysulfonating a microporous polymer ion exchange resin to produce a polysulfonated ion exchange resin, pyrolyzing the polysulfonated ion exchange resin to produce the carbonaceous adsorbent, activating the carbonaceous adsorbent to form an activated carbonaceous adsorbent, and pyrolyzing the activated carbonaceous adsorbent to form the carbon molecular sieve.

[0015] In yet another additional embodiment, a method for forming a carbon molecular is provided that includes contacting a porous polymer ion exchange resin with an amount of fuming sulfuric acid ranging from about 100% to about 2000% of the total weight of the ion exchange resin at a temperature ranging from about 100° C to about 180° C for a period ranging from about five hours to about 72 hours to form a polysulfonated ion exchange resin. The method further includes pyrolyzing the polysulfonated ion exchange resin at a temperature ranging from about 300° C to about 1200° C for a period ranging from about 15 minutes to about two hours to form a carbonaceous adsorbent. Additionally, the method includes contacting the carbonaceous adsorbent with steam at a temperature ranging from about 500° C to about 1200° C to form an activated carbonaceous adsorbent. This method also includes pyrolyzing the activated carbonaceous adsorbent at a temperature ranging from about 560° C to about 1300° C for a period of about 15 minutes to about two hours to form the carbon molecular sieve.

[0016] Another embodiment provides a method for separating an amount of a molecular gas chosen from hydrogen, helium, xenon, krypton, methane,

ethane, carbon monoxide, carbon dioxide, or any combination thereof from a mixture of gases. The method includes contacting the mixture of gases with a carbon molecular sieve particle at a pressure ranging from about 1 psig and about 1000 psig. The carbon molecular sieve particle includes an essentially spherical particle comprising carbon equal to or greater than about 99% by weight of the particle. The particle has a diameter ranging from about 2  $\mu\text{m}$  to about 1000  $\mu\text{m}$ . Each carbon molecular sieve particle also includes a plurality of micropore sidewalls forming interconnected micropores having internal diameters ranging from about 10  $\text{\AA}$  to about 20  $\text{\AA}$ . The micropore sidewalls comprise from about 5% to about 40% of the total surface area of the carbon molecular sieve particles. Each carbon molecular sieve particle also includes a plurality of ultramicropore sidewalls forming ultramicropores having internal diameters ranging from about 4.5  $\text{\AA}$  to about 5.5  $\text{\AA}$ . The ultramicropore sidewalls comprise from about 10% to about 60% of the total surface area of the carbon molecular sieve particles.

[0017] An additional embodiment provides a method for separating an amount of a molecular gas chosen from hydrogen, helium, xenon, krypton, methane, ethane, carbon monoxide, carbon dioxide, or any combination thereof from a mixture of gases that includes the molecular gas. The method includes contacting the mixture of gases with a carbon molecular sieve particle at a pressure ranging from about 1 psig and about 1000 psig. Each carbon molecular sieve particle includes an essentially spherical particle comprising carbon equal to or greater than about 99% by weight of the particle. The particle has a diameter ranging from about 2  $\mu\text{m}$  to about 1000  $\mu\text{m}$ . The carbon molecular sieve particle also includes a plurality of micropore sidewalls forming interconnected micropores having internal diameters ranging from about 10  $\text{\AA}$  to about 20  $\text{\AA}$ . The micropore sidewalls comprise from about 5% to about 40% of the total surface area of the carbon molecular sieve particle. In addition, each carbon molecular sieve particle includes a plurality of ultramicropore sidewalls forming ultramicropores having internal diameters ranging from about 4.5  $\text{\AA}$  to about 5.5  $\text{\AA}$ . The ultramicropore sidewalls comprise from about 10% to about 60% of the total surface area of the carbon molecular sieve particle.

[0018] Additional objectives, advantages and novel features will be set forth in the description which follows or will become apparent to those skilled in the art upon examination of the drawings and detailed description which follows.

**DESCRIPTION OF THE FIGURES**

[0019] FIG. 1 is a graph summarizing the distribution of surface area in the interior of micropores and ultramicropores in three carbon molecular sieve materials fabricated in accordance with the embodiments of the present invention.

[0020] FIG. 2 is a graph summarizing the PCT measurements as % wt of hydrogen stored as a function of hydrogen pressure in the sample container.

[0021] FIG. 3 is a graph of the %wt of hydrogen stored by a carbon molecular sieve sample during two adsorption/desorption cycles.

[0022] Corresponding reference characters indicate corresponding elements among the view of the drawings. The headings used in the figures should not be interpreted to limit the scope of the claims.

**DETAILED DESCRIPTION OF THE INVENTION**

[0023] The present invention relates to a composition and method of making a composition used to adsorb and store hydrogen and other light gases. More specifically, the present invention provides a carbon molecular sieve (CMS) and a method of making a CMS. Further, a method of storing and releasing hydrogen, as well as adsorbing other light gases is provided.

[0024] The CMS may be a synthetic polymer carbon that includes a substantial percentage of ultramicropores. The ultramicropores may have a mean internal diameter of less than about 7 Å. The internal diameters of the ultramicropores may fall inside a narrow range, typically within  $\pm 0.5$  Å of the mean internal diameter of the ultramicropores. Without being bound to any particular theory, the narrow range of ultramicropore diameters may make the CMS particles capable of adsorbing a single species of small gas compound to the exclusion of other small gas compounds that differ in molecular size.

[0025] A description of embodiments of the CMS, methods of producing the CMS, methods of using the CMS to store and release hydrogen, and methods to adsorb hydrogen and other light gases are presented in detail below.

## **I. Carbon Molecular Sieves**

[0026] In an embodiment, the carbon molecular sieve (CMS) comprises a partially pyrolyzed polysulfonated microporous carbon polymer. The polymer comprises about 99% carbon and about 1% hydrogen by weight. A plurality of CMS may be combined for use. In an embodiment, each CMS may be an essentially spherical particle ranging in size from about 2  $\mu\text{m}$  to about 1000  $\mu\text{m}$ . In another embodiment, each CMS may range in size from about 2  $\mu\text{m}$  to about 500  $\mu\text{m}$ , from about 250  $\mu\text{m}$  to about 750  $\mu\text{m}$ , or from about 500  $\mu\text{m}$  to about 1000  $\mu\text{m}$ . The size of each CMS may be specified by the control of specific aspects of the fabrication process, described below.

[0027] The CMS may have a latticework that forms a plurality of interconnected micropores; the walls of the interconnected micropores may further contain a plurality of ultramicropores. Typically, the micropores having mean pore diameters greater than about 10  $\text{\AA}$  may be located predominantly near the exposed exterior surface of the CMS particle. The ultramicropores having mean internal diameters less than about 10  $\text{\AA}$  may be located within the walls of the interconnected micropores in the interior of the CMS particles. Aspects of the fabrication process, such as those described below, may control the distribution of pore sizes.

[0028] Without being bound to any particular theory, the larger outer micropores may allow for the effective mass transfer of small adsorbate molecules to the ultramicropores and to prevent the fouling of the ultramicropores by larger molecules. The small adsorbate molecules such as hydrogen or methanol may condense in the ultramicroporous regions.

### **A. Surface Area of CMS**

[0029] Because the CMS captures small molecules such as hydrogen by a process of adsorption, in which the molecule to be captured interacts with the surface of the CMS, surface area is one feature that may directly impact the performance of the CMS during its use. A higher surface area per gram of CMS particles may lead to more available surface area on the CMS particles for adsorptive processes. The total surface area of the CMS may be subdivided from the total area of the sidewalls of the ultramicropores, the total area of the sidewalls of the micropores, and the exposed outer surface of the CMS not occupied by

micropores or ultramicropores. A higher percentage of total surface area comprising the sidewalls of the ultramicropores may indicate that the CMS includes more ultramicropores. Because small molecules such as hydrogen may condense specifically within ultramicropores, the percentage of the total surface area of the CMS comprising the walls of ultramicropores may be another factor that impacts the capacity of the CMS to adsorb small molecules.

[0030] The total surface area of the CMS may range from about 300m<sup>2</sup> per g of CMS particles and about 3500m<sup>2</sup> per g of CMS particles. The total surface area may range from about 300m<sup>2</sup> per g of CMS particles to about 2000m<sup>2</sup> per g of CMS particles, from about 1500m<sup>2</sup> per g of CMS particles to about 2500m<sup>2</sup> per g of CMS particles, and from about 2000m<sup>2</sup> per g of CMS particles to about 3500m<sup>2</sup> per g of CMS particles.

[0031] In an embodiment, the sidewalls of the micropores of the CMS may comprise from about 5% to about 40% of the total surface area of the CMS. In other embodiments, the sidewalls of the micropores of the CMS may comprise from about 5% to about 15%, from about 10% to about 20%, from about 15% to about 25%, from about 20% to about 30%, from about 25% to about 35%, and from about 30% to about 40% of the total surface area of the CMS. In an additional embodiment, the sidewalls of the ultramicropores comprise from about 10% to about 60% of the total surface area of the CMS. In other additional embodiments, the sidewalls of the ultramicropores comprise from about 10% to about 20%, from about 15% to about 25%, from about 20% to about 30%, from about 25% to about 35%, from about 30% to about 40%, from about 35% to about 45%, from about 40% to about 50%, from about 45% to about 55%, and from about 50% to about 60% of the total surface area of the CMS. The remaining percentage of the total surface area of the CMS includes the exposed external surface of the CMS.

### ***B. Ultramicropore Internal Diameters***

[0032] The mean internal diameters of the ultramicropores of the CMS may range from about 3 Å and about 10 Å. In addition, the internal diameter of individual ultramicropores of the CMS may fall within about  $\pm 0.5$  Å of the mean diameter of all ultramicropores of the CMS. Without being bound to any particular theory, the internal diameters of the ultramicropores may determine the specific

small molecule species that adsorbs into a given CMS and condenses inside of its ultramicropores. Generally, smaller ultramicropores adsorb smaller molecules. In order to enhance the specificity of a CMS for a particular species of molecule, the range of internal diameters of the ultramicropores may be selected to fall within a relatively narrow range. For example, CMS particles in which essentially all of the ultramicropores range in internal diameter from about 4.5 Å and about 5.5 Å may possess a strong affinity for adsorbing molecular hydrogen. CMS particles in which the mean internal diameter of the ultramicropores is slightly larger may adsorb slightly larger molecules with high selectivity, so long as the variation in the diameter falls within about  $\pm 0.5$  Å of the mean diameter of all ultramicropores of the CMS.

[0033] The mean internal diameters of the ultramicropores of the CMS may range from about 3 Å and about 4 Å, about 3.5 Å and about 4.5 Å, about 4 Å and about 5 Å, about 4.5 Å and about 5.5 Å, about 5 Å and about 6 Å, and about 5.5 Å and about 6.5 Å, or about 6 Å and about 7 Å.

### **C. Surface Chemistry of CMS Particles**

[0034] The CMS particles may typically comprise about 99% carbon and about 1% hydrogen. The carbon atoms may be arranged in sheet-like complexes of interconnected 6-carbon rings, and each 6-carbon ring may include from one and three double bonds from adjacent carbon atoms. The surface of the CMS particles may include carbon atoms that possess predominantly  $sp^3$  orbitals, likely due to the extensive double bonding from adjacent carbon atoms. The surface of the CMS particles may be relatively hydrophobic as a result of this structure.

## **II. Method of Producing CMS**

[0035] CMS particles may be prepared by the pyrolysis of an ion exchange resin (IER). A macroporous polymer may be synthesized using a suspension polymerization process, functionalized to obtain a sulfonated IER, and then the sulfonated IER may be pyrolyzed to obtain carbonaceous particles. Without being bound to any particular theory, the novel step of sulfonating the IER prior to the pyrolysis may maintain the porous structure of the resulting carbonaceous particle. Without prior sulfonation, the pores of the IER may collapse during pyrolysis, yielding an essentially non-porous CMS particle.

[0036] The carbonaceous particles may undergo further treatments such as steam activation and additional pyrolysis in order to impart predetermined properties to the CMS particles. For example, additional pyrolysis may be performed on the carbonaceous particles at a predetermined temperature profile in order to adjust the mean diameter of the ultramicropores to a desired value.

#### **A. Suspension Polymerization**

[0037] The ion exchange resin (IER) is synthesized using known suspension polymerization methods similar to the processes described in U.S. Patent numbers 4,256,840 and 4,224,415. In an embodiment, the IER may be formed by the polymerization of a mixture of monomers suspended in an aqueous phase. The IER may be a macroporous vinylaromatic polymer, similar to the polymers and copolymers described in U.S. Patent 4,839,331. In brief, a monomer mix and an aqueous phase may be contacted and stirred together at about 75° C for from about 12 hours and about 24 hours, forming polymer particles in aqueous suspension. The aqueous phase and monomer mix may be stirred together at a constant speed ranging from about 200 rpm and about 2000 rpm. The polymer particles may be synthesized to a predetermined particle size by stirring at a specified stirring speed; a higher stirring speed results in smaller polymer particles.

[0038] After stirring, the suspended polymer particles may be cooled and rinsed with an organic solvent. The organic solvent may be any low-boiling point solvent, including but not limited to methanol, acetonitrile, and combinations thereof. For example, acetonitrile may be added to the room temperature suspension polymerization mixture and stirred at a speed of about 500 rpm for about one hour. In addition, the polymer may be filtered and rinsed with the organic solvent described above. For example, the rinsed polymer may be filtered using a vacuum filtration unit with a 20-50  $\mu\text{m}$  glass frit funnel, and the polymer remaining in the filter may be rinsed with excess acetonitrile.

[0039] As a non-limiting example, the suspension polymerization of an IER may be performed by forming a monomer mix containing monomers such as devinylbenzene, a polymerization initiator such as butyl peroctate, and a phase extender such as toluene. This monomer mix may be contacted with an aqueous phase containing deionized water, less than 1% by weight of the aqueous phase of a

surfactant such as dodecylsulfate, less than 1% by weight of the aqueous phase of a high molecular weight suspension particle stabilizer such as culminal, and an aqueous phase charging molecule such as boric acid, to form a suspension polymerization mixture. Sodium hydroxide may be added to the suspension polymerization mixture while stirring to adjust the pH of the mixture to about 9.25.

[0040] The monomers may be stabilized in the deionized water and surfactant, whereas the relatively insoluble polymer may remain in the suspended environment due to interactions with the surfactant and suspension particle stabilizer compounds in solution with the polymer. The monomer mix may form into droplets upon contact with the aqueous phase. The polymerization reactions may take place within the droplets of monomer mixture.

[0041] As the monomers polymerize, they may remain suspended in the aqueous solution, and may additionally repel any residual deionized water from within the suspended polymeric particles. Within each droplet, the phase extender, within which the monomers are soluble, may maintain the monomers in suspension prior to polymerization. However, the polymer may not be soluble within the phase extender. As a result, as the monomers are polymerized into the IER polymer, the phase extender may be forced out of the polymer, leaving behind a plurality of interconnected pores in the IER polymer. The volume occupied by the phase extender may maintain voids within the polymer as it is forming, resulting in the formation of pores within the polymeric IER particles.

[0042] The material of the polymeric particle may form a lattice-like structure containing a plurality of interconnected pores and micropores. During pyrolysis, the pores and micropores may decrease in diameter to form the interconnected micropores and ultramicropores of the CMS particles.

## **1. aqueous phase**

[0043] The aqueous phase, in addition to deionized water, may contain other additives including aqueous phase charging molecules, surfactants, suspension stabilizers, pH-increasing compounds, and pH-decreasing compounds.

[0044] Deionized water in the aqueous phase may act as a solvent in which the polymerization reactions occur, and may also act as a heat sink to help dissipate the heat generated by the exothermic polymerization reactions. The

particular additives included in the aqueous phase may vary depending on the composition of the monomer mix and the desired properties of the polymerization reaction and resulting IER.

[0045] Aqueous phase charging molecules may help to keep the phase extender in the monomer mix within the polymer particles. Non-limiting examples of aqueous phase charging molecules include boric acid, sodium carbonate, sodium bicarbonate, and combinations thereof.

[0046] The surfactants may induce the formation of micelles within which polymerization occurs. Any anionic surfactant compound may be used as a surfactant, including but not limited to dodecyl sulfate, perfluorooctanoate, perfluorooctanesulfonate, alkyl sulfate salts such as sodium dodecyl sulfate and ammonium lauryl sulfate, sodium lauryl ether sulfate, alkyl benzene sulfonate, and other fatty acid salts.

[0047] Suspension stabilizers may be added to the aqueous phase to suspend both the monomer and polymer in the aqueous solvent. Non-limiting examples of suspension stabilizers include cuminal, and any high molecular weight cellulose, including but not limited to hydroxymethylcellulose.

[0048] In an embodiment, the aqueous phase may include dodecyl sulfate as a surfactant, cuminal as a suspension stabilizer, and boric acid as an aqueous phase charging molecule. In general, the total amount of additives included in the aqueous phase may amount to less than about 1% of the total mass of the aqueous phase. In one embodiment, the aqueous phase includes 99.4% deionized water, about 0.4% boric acid, about 0.15% cuminal, and about 0.05% dodecyl sulfate by weight.

## **2. monomer mix**

[0049] In an embodiment, the monomer mix contains the monomers to be polymerized, along with a polymerization initiator. In addition, the monomer mix may contain a phase extender used to introduce pores into the ion exchange resin (IER) during polymerization.

[0050] The monomer mix may include at least one monomer compound, including but not limited to polyvinylidene compounds, monovinylidene monomers, monoethylenically unsaturated monomers and combinations thereof.

Non-limiting examples of suitable polyvinylidene compounds include divinylbenzene, divinylpyridine, divinyltoluene, divinyl naphthalene, diallyl phthalate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, divinylxylene, divinylethylbenzene, divinylsulfone, polyvinyl ethers of glycol, polyallyl ethers of glycol, polyvinyl ethers of glycerol, polyallyl ethers of glycerol, polyvinyl ethers of pentaerythritol, polyallyl ethers of pentaerythritol, polyvinyl ethers of resorcinol, polyallyl ethers of resorcinol, divinylketone, divinylsulfide, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl carbonate, diallyl malonate, diallyl oxalate, diallyl adipate, diallyl sebacate, divinylsebacate, diallyl tartrate, diallyl silicate, triallyl tricarballylate, triallyl aconitate, triallyl citrate, triallyl phosphate, N,N'-methylenediacrylamide, N,N'-methylene dimethacrylamide, N,N'-ethylenediacrylamide, 1,2-di(.alpha.-methylmethylene sulfonamido)ethylene, trivinylbenzene, trivinyl naphthalene, and polyvinylanthracenes. Non-limiting examples of suitable monovinylidene monomers include vinylpyridine, 2-methyl-5-vinylpyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, and 2-methyl-3-ethyl-5-vinylpyridine, 2-methyl-5-vinylquinoline, 4-methyl-4-vinylquinoline, 1-methyl- or 3-methyl-5-vinylisoquinoline and vinylpyrrolidone. Non-limiting examples of suitable monoethylenically unsaturated monomers include styrene, acrylonitrile, methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, tert-butyl acrylate, ethylhexyl acrylate, cyclohexyl acrylate, isobornyl acrylate, benzyl acrylate, phenyl acrylate, alkylphenyl acrylate, ethoxymethyl acrylate, ethoxyethyl acrylate, ethoxypropyl acrylate, propoxymethyl acrylate, propoxyethyl acrylate, propoxypropyl acrylate, ethoxyphenyl acrylate, ethoxybenzyl acrylate, ethoxycyclohexyl acrylate, and the corresponding esters of methacrylic acid, vinyltoluene, and vinyl naphthalene.

[0051] Polymerization initiators may be included in the monomer mix in an amount ranging from about 0.01% and about 3% of the weight of monomers. Non-limiting examples of polymerization initiators include butyl peroxide, benzoyl peroxide, tert-butyl hydroperoxide, cumene peroxide, tetralin peroxide, acetyl peroxide, caproyl peroxide, tert-butyl perbenzoate, tert-butyl diperphthalate, and methyl ethyl ketone peroxide.

[0052] The monomer mix may additionally include a phase extender to create and maintain pores during polymerization. Phase extender, as defined

herein, refer to compounds within which the monomers to be polymerized are soluble, but within which the polymer is not soluble. Non-limiting examples of phase extender compounds include toluene, xylene, ethylbenzene, C<sub>6</sub> - C<sub>12</sub> saturated aliphatic hydrocarbons including heptane and iso-octane, C<sub>4</sub> - C<sub>10</sub> alkanols including tert-amyl alcohol, sec-butanol and 2-ethylhexanol, and primary alcohols.

[0053] The amount of phase extender included in the monomer mix may range from about 20% and about 60% of the total weight of the monomer mix. The amount and composition of phase extender included in the monomer mix may influence the size and amount of pores in the polymer mix. For example, a higher amount of toluene in the monomer mix may result in a higher number of larger pores in the resulting polymer.

[0054] The amount and composition of monomer compounds, as well as the composition and amount of phase extender included in the monomer mix may be manipulated in order to synthesize polymer particles having a predetermined size and number of pores. Monomer mix compositions having a higher percentage of phase extender may yield polymer particles with larger and more numerous pores. Monomer mixes containing relatively high proportions of extensively cross-linkable polymers such as divinylbenzene may yield polymers with smaller and less numerous pores than monomer mixes containing less cross-linkable monomers such as styrene.

[0055] In an embodiment, the monomer included in the monomer mix is divinylbenzene and the polymerization initiator is butyl peroctate, in a combined amount ranging from about 0.1% and about 5% of the total mass of the monomer mix. In another embodiment, the monomer mix may additionally include toluene as a phase extender in an amount ranging from about 0.1% and about 50% of the total mass of the monomer mix. In an additional embodiment, the monomer mix may include about 66% divinylbenzene, about 33% toluene, and about 1% butyl peroctate by weight.

### **B. Polysulfonation**

[0056] The ion exchange resin (IER) particles synthesized by the processes described above may be functionalized by a process of polysulfonation, defined herein as the process of introducing an average of more than one sulfonate

group to each accessible aromatic nucleus within the polymer particles. The process of polysulfonation may stabilize the pore structure of the polymer particles, and may further prevent the pores from total collapse during subsequent pyrolysis of the polymer particles.

[0057] Polysulfonation of the IER may be achieved by contacting the IER resulting from the processes described above with an amount of fuming sulfuric acid for a period ranging from about five hours to about 72 hours at a temperature ranging from about 100° C and about 180° C. The amount of fuming sulfuric acid may range from about 100% and about 2000% of the total weight of the IER particles.

[0058] Fuming sulfuric acid, as defined herein, refers to a solution of sulfur trioxide in sulfuric acid. When contacted with the IER, both sulfonate and sulfone groups may covalently bind to available carbons in the IER. In addition, sulfone crosslinks may form from non-crosslinked carbons in the IER.

[0059] In an embodiment, the polymer particles are contacted with fuming sulfuric acid in an amount of 500% of the weight of the polymer particles by drop-wise addition over a period of 48 hours at room temperature, then shaking the polymer particles in the acid at a temperature of about 150° C for about four hours.

[0060] After the completion of polysulfonation, the polymer particles may be neutralized by rinsing the particles in deionized water, while maintaining the temperature of the mixture of water and particles below about 100° C.

[0061] The polysulfonated IER particles may exhibit enhanced stabilization of the polymer during pyrolysis as compared to IER particles that have been monosulfonated using sulfuric acid. The outgassing of the sulfur complexes during pyrolysis may contribute to higher pore volume that more closely resembles the pore structure of the desired carbonaceous adsorbent particles.

### **C. Pyrolysis**

[0062] The polysulfonated IER polymer particles synthesized by the processes described above may be subjected to pyrolysis in order to produce carbonaceous adsorbent particles. Prior to pyrolysis, the porous polysulfonated IER particles may comprise networks of extensively cross-linked carbon rings saturated with attached sulfonate and sulfone groups, as well as sulfone cross-links. Pyrolysis

may induce the outgassing of essentially all of the attached sulfonate and sulfone groups, forming carbonaceous adsorbent particles. The carbonaceous adsorbent particles resulting from pyrolysis may comprise extensively crosslinked carbon rings in an approximately graphite-like structure, and may further contain a plurality of micropores, mesopores, and macropores, depending on the composition and amount of phase extender included in the monomer mix.

[0063] In an embodiment, pyrolysis is performed at a temperature ranging from about 300° C and about 1200° C for a period ranging from about fifteen minutes and about two hours. A fluidized bed treatment may be used for the pyrolysis, defined herein as a process in which heated nitrogen is passed upward through a bed of polysulfonated polymer particles, and in which the gas serves to agitate as well as to heat the particles. A static bed may also be used for pyrolysis.

[0064] For example, a batch of polysulfonated IER polymer particles may be loaded into quartz trays and loaded into a Thermcraft oven and heated to a temperature of about 1100° C for about two hours. The resulting carbonaceous particles may be removed from the Thermcraft oven after cooling the oven to room temperature.

#### ***D. Steam Activation and Other Activation Processes***

[0065] The carbonaceous particles synthesized by the processes described above may be steam activated at temperatures ranging from about 500° C and about 1200° C. Steam activation may widen the micropores within the carbonaceous particles by a process in which the water vapor dissociates and reacts with the carbonaceous particles. The oxygen component of the dissociated steam may react with carbon in the framework of the carbonaceous particles to form CO<sub>2</sub>, which outgases from the particles. The steam activation process may create new pores by the removal of carbon from the carbonaceous particles, and may also reopen pores closed by the initial pyrolysis process described above. Any adsorbed compounds trapped within the pores of the particles may be solubilized and removed from the particles during the steam activation process.

[0066] In an embodiment, the steam activation process is performed by placing the carbonaceous particles in a Lindberg vertical furnace and attaching a source of steam to the inlet line of the furnace. The steam activation process may

be performed for a period of time sufficient to ensure that the maximum number of pores has opened up in the carbonaceous material, and to ensure that the desired micropore diameter is achieved.

[0067] The size of the pores within the carbonaceous particles may be manipulated to predetermined values by specifying the duration and temperature at which the steam activation is performed. Longer durations and higher activation temperatures may be associated with larger and more numerous pores in the carbonaceous particles.

[0068] In another embodiment, the steam activation of the carbonaceous particles may be conducted at a temperature ranging from about 550° C and about 1000° C. In an additional embodiment, the steam activation of the carbonaceous particles may be conducted at a temperature of about 850° C.

[0069] In another additional embodiment, other activation processes including but not limited to liquid-phase activation, chemical activation, compressed air activation, or any combination thereof may be employed to activate the carbonaceous particles. Non-limiting examples of physical activation gases suitable for use in an activation process include steam, oxygen, and carbon dioxide.

#### ***E. Post-Activation Pyrolysis***

[0070] The activated carbonaceous particles may be subjected to a second pyrolysis treatment to reduce the overall size of the pores within the particles. The desired overall size of the pores within the particles may be selected to impart specificity for the adsorption of particular compounds based on the internal diameter of the ultramicropores. The resulting internal diameters of the pores within the carbonaceous particles after post-activation pyrolysis may depend upon the temperature and duration at which the pyrolysis is conducted. Upon completion of the post-activation pyrolysis, the resulting carbon molecular sieve particles may be suitable for use.

[0071] In an embodiment, the post-activation pyrolysis is conducted at a temperature ranging from about 560° C and about 1300° C. In another embodiment, the post-activation pyrolysis is conducted at a temperature of about 1150° C.

### ***III. Method of Storing and Releasing Molecular Hydrogen***

[0072] The present invention provides a method of storing and releasing molecular hydrogen. This method may include providing an amount of carbon molecular sieve (CMS) particles with a plurality of ultramicropores having an average internal diameter of about 5 Å, and in which the internal diameters of individual ultramicropores range from 4.5 Å and 5.5 Å.

[0073] The CMS particles may be contacted with molecular hydrogen at a pressure ranging from about 1 psig and about 1000 psig. The CMS particles may be placed in a container capable of holding the hydrogen gas at pressures ranging from about 1 psig and about 1000 psig. As the pressure of the molecular hydrogen increases, the molecular hydrogen may condense inside of the ultramicropores of CMS, causing the molecular hydrogen to be stored inside of the ultramicropores of the CMS. The temperature at which the molecular hydrogen may be contacted with the CMS particles may range from about 20K and about room temperature. When the pressure of the molecular hydrogen contacting the CMS particles is reduced, or the temperature of the CMS particles is increased, or any combination thereof, the hydrogen condensed in the ultramicropores of the CMS may be released back to the surrounding atmosphere. The CMS particles may store and release molecular hydrogen using the method described above an unlimited number of times.

[0074] The excess capacity of the CMS particles may vary depending on any one or more factors including but not limited the temperature and pressure of the molecular hydrogen contacted with the CMS particles. The maximum excess capacity of the CMS particles may range from about 1.5% and about 3.5% by weight.

[0075] The CMS particles may be capable of storing molecular hydrogen that includes a minor amount of impurities. However, over numerous storage/release cycles of molecular hydrogen containing impurities, the accumulated condensation of impurities in the CMS particles may adversely affect the excess capacity of the CMS particles. Re-activating and re-pyrolyzing the CMS particles using methods similar to those described above may regenerate the CMS particles. The regeneration of the CMS particles may be repeated numerous times as needed throughout the duration of use of the CMS particle.

#### ***IV. Method of Adsorbing Small Molecules***

[0076] The present invention provides a method of adsorbing small airborne molecules using the CMS particles described above. This method may include providing an amount of carbon molecular sieve (CMS) particles with a plurality of ultramicropores having an average internal diameter from about 3 Å and about 7 Å, and in which the range of internal diameters of the ultramicropores is less than about 1 Å. The internal diameter of the ultramicropores may be sized to optimize the affinity of the CMS particles for a particular small airborne molecule. A CMS particle containing ultramicropores with larger internal diameters may have an affinity for larger airborne molecules.

[0077] Non-limiting examples of small airborne molecules that may be adsorbed using the CMS particles include hydrogen, helium, xenon, krypton, methane, ethane, carbon monoxide, and other light gases.

[0078] In an embodiment, the CMS particles are contacted with a gas containing the small airborne molecules at a pressure ranging from about 1 psig and about 1000 psig. As the pressure of the gas increases, the small airborne molecules may condense inside of the ultramicropores of CMS, causing the small airborne molecules to be stored inside of the ultramicropores of the CMS. The temperature at which the gas may be contacted with the CMS particles may range from about 20K and about room temperature.

[0079] In another embodiment, the CMS particles may be used to separate a desired gas, including but not limited to hydrogen or helium, from a gas mixture including the desired gas and at least one additional gas. In this embodiment, the CMS particles may be contacted with the gas mixture at a pressure ranging from about 1 psig and about 1000 psig, causing the adsorption of the desired gas into the ultramicropores of the CMS particles.

[0080] For example, a packed bed of CMS particles may be included in a pressure-swing adsorption system. In the pressure-swing adsorption system, a pressurized gas mixture containing a desired gas, including but not limited to hydrogen and helium, may be passed through a packed bed of CMS particles, causing the adsorption of the desired gas into the ultramicropores of the CMS particles. The desired gas may be released from the CMS particles in the pressure-

swing adsorption system by reducing the pressure on the packed bed of CMS particles, causing the release of the adsorbed gas from the ultramicropores of the CMS particles. The cycle of pressurization and depressurization of the bed of CMS particles may be repeated at least one time to separate an amount of the desired gas from the gas mixture.

## **V. DEFINITIONS**

[0081] To facilitate understanding of the invention, a number of terms and abbreviations as used herein are defined below:

[0082] The term "macropore" generally refers herein to pores having an internal diameter greater than about 500 Å.

[0083] The term "mesopore" generally refers herein to pores having an internal diameter from about 20 Å and about 500 Å.

[0084] The term "micropore" generally refers herein to pores having an internal diameter from about 10 Å and about 20 Å.

[0085] The term "ultramicropore" generally refers herein to pores having an internal diameter of less than about 10 Å.

## **EXAMPLES**

[0086] The following examples illustrate embodiments of the invention.

### **Example 1. Fabrication of Carbon Molecular Sieve Material.**

[0087] To demonstrate the feasibility of fabricating a carbon molecular sieve material by the pyrolysis of an ion exchange resin, the following experiment was conducted. Initially, a microporous polymer was synthesized using a suspension polymerization process and then functionalized to obtain a sulfonated ion exchange resin. The ion exchange resin was then pyrolyzed, steam activated, and then further pyrolyzed, yielding the carbon molecular sieve material.

[0088] The suspension polymerization process combined an aqueous phase with a monomer mix to yield the ion exchange resin. The aqueous phase and monomer mix were mixed separately, and later combined and rinsed.

[0089] To make the aqueous phase, the following compounds were weighed into a 4L Erlenmeyer flask: 4.21875g culminal, 1.3875g dodecyl sulfate,

11.03125g boric acid, and 2780.625g of deionized water. The flask was sealed with aluminum foil and stirred on a magnetic stir plate for 16 hours.

[0090] A 12L round bottom synthesis flask with a 71/60 center neck, and two 45/50 necks was placed in a heating mantle, a temperature probe was inserted into the synthesis flask, and a four-blade Teflon paddle in the flask was connected to a mixing motor. The aqueous phase in the 4L Erlenmeyer flask was transferred to the three-neck synthesis flask and the height of the Teflon paddle was adjusted to one inch above the bottom of the synthesis flask. While stirring at 500 rpm, a 50% solution of NaOH by weight was slowly pipetted into the synthesis flask until a pH of  $9.25 \pm 0.25$  was achieved.

[0091] A monomer mix made up of 18.50g butyl peroctate, 500g toluene and 1000g divinylbenzene was weighed into a 2L Erlenmeyer flask, and added to the aqueous phase in the synthesis flask. The rate of stirring was increased to 1000 rpm and the mixture was slowly heated to a temperature of 72° C and held at this temperature for sixteen hours. The resulting ion exchange resin was then cooled to room temperature while continuing to stir at 1000 rpm.

[0092] The cooled resin was then rinsed by adding methanol to the synthesis flask in an amount sufficient to fill the flask while stirring at 500 rpm for one hour. After mixing, the mix motor was stopped and the resin was allowed to settle to the bottom of the synthesis flask. The methanol was decanted off of the top of the contents of the synthesis flask and discarded. The resin remaining in the synthesis flask was vacuum filtered through a large glass funnel with a 20-50  $\mu\text{m}$  frit. The resin remaining in the glass funnel was then rinsed with 8L of fresh methanol.

[0093] A large spatula was used to scoop the semi-dried caked resin into Pyrex pie plates. The pie plates were covered with aluminum foil and transferred into a vacuum oven and dried under full vacuum at 80° C for sixteen hours.

[0094] The dried resin was then polysulfonated using fuming sulfuric acid. The resin was transferred to a 12L round bottom flask with 20/40 joints and mounted on an orbital shaker in a heating mantle. A water condenser, a temperature probe, and a 1000ml addition funnel were attached to the flask. After starting the water condenser, fuming sulfuric acid was added to the flask drop-wise through the addition funnel for 48 hours, while maintaining the mixture at room

temperature. After an amount of fuming sulfuric acid totaling 5mL/g of resin had been added, the addition funnel was replaced by a glass stopper. The mixture was then heated to 150° C and shaken at 75 rpm for 4 hrs.

[0095] The mixture was then neutralized by cooling to room temperature and then slowly adding deionized water to fill the 12L flask. Additional deionized water was added to the flask via the water supply tube, slowly and periodically pushing the water supply tube into the bed of sulfonated resin at the bottom of the flask until the bottom of the flask apparatus was reached, while maintaining the temperature of the mixture below 100° C. After decanting and discarding the deionized water from the top of the flask, the remaining resin material was poured into a 10L poly bucket and allowed to settle to the bottom of the bucket.

[0096] Deionized water was continuously supplied to the poly bucket, and the overflow was discarded. The resin was occasionally stirred while supplying additional deionized water, until the pH of the resin returned to neutral.

[0097] The resin was then scooped out into Pyrex pie plates and air-dried in a laboratory hood for several days, stirring occasionally with a large spatula. After drying, the entire batch of resin was pyrolyzed by loading the resin into a quartz combustion tray, placed in a horizontal oven (Thermcraft) and heated using the temperature profile listed in Table 1. After the horizontal oven had cooled to room temperature, the resin was removed and transferred to a glass jar.

TABLE 1: Initial Pyrolysis Temperature Profile

Elapsed Time (hr)	Oven Temperature Set Point (°C)
0	200
1.0	500
2.5	825
4.5	off

[0098] The material in the glass jar was shaken through stacked 12" testing sieves (170 and 635 mesh) by shaking one half of the material at a time in the sieves for two fifteen-minute cycles, unbinding the screens from each cycle. The 170/635 mesh fraction of the material was loaded into a 7" quartz combustion tube with a #3 size frit in the middle.

[0099] After adding quartz wool over the material, the combustion tube was placed in a vertical Lindberg furnace with a nitrogen flow rate of 1L/min. Deionized water in a 1000mL 3-neck boiling flask was heated, starting at room temperature. During heating, the temperature of the deionized water was monitored. When the water temperature in the boiling flask had reached 50° C, the resulting steam was connected to the inlet line of the combustion tube, the vertical oven was set to a temperature of 840°C and the oven was started. The temperature of the deionized water in the boiling flask was further increased to 85° C and maintained at this temperature throughout the steam activation procedure. After the oven had reached 840°C, the countdown timer of the temperature program controller was started. The temperature profile commanded by the countdown timer is summarized in Table 2.

TABLE 2: Steam Activation Temperature Profile

<b>Elapsed Time (hr)</b>	<b>Oven Temperature Set Point (°C)</b>
0	500
0.75	850
4	off

[0100] Once the furnace program had completed, the combustion tube was disconnected from the oven and the adsorbent was rapidly cooled to room temperature. The overall process yielded a carbonaceous adsorbent with a surface area of about 1000-1300m<sup>2</sup>/g of material.

[0101] The adsorbent was then subjected to a second round of pyrolysis at a temperature of 1150° C using methods similar to those described above. The resulting carbon molecular sieve material had a significant amount of incremental surface area attributable to ultramicropores with an internal diameter of less than about 7 Å, as shown in FIG. 1.

[0102] The results of this experiment demonstrated the feasibility of fabricating a CMS material that contained a significant number of ultramicropores with a narrow range of internal diameters.

**Example 2. Hydrogen Adsorption Capacity of Carbon Molecular Sieve****Material.**

[0103] To demonstrate the capacity of a carbon molecular sieve material for the adsorption and storage of hydrogen, the following experiments were conducted.

[0104] A 4.515 g sample of a CMS material produced using methods similar to those described in Example 1 was loaded into a sample holder and connected to a Sieverts gas sorption instrument (Hy-Energy model PCTPro-2000, HY-Energy, LLC, Newark, CA, USA) using a 1/16-inch tube with a 0.5-micron fritted filter nickel VCR gasket.

[0105] At a temperature of 30° C, the instrument lines were purged of air using three helium flush/evacuation cycles. The free gas volume in the sample holder was auto-calibrated using helium; the measured free gas volume in the sample holder was  $10.382 \pm 0.1029$  ml (mean  $\pm$  std dev). The volume of the CMS sample was estimated by subtracting the measured free volume within the sample container from the total volume of the sample container. This estimated CMS sample volume was within 0.65% of the volume estimated from the measured mass and known skeletal density of the CMS sample.

[0106] After activating the CMS sample in the sample container under vacuum for 3 hours at 300° C, the CMS sample was subjected to PCT measurements using the Sieverts gas sorption instrument. Two adsorption and desorption PCT isotherms were obtained at a temperature of -196 ° C using pressures ranging from 0.001 to 90 bar in 10 bar pressure increments. A calibrated reservoir with a volume of 11.71 ml was used for the PCT measurements. A sample of an inert material with similar skeletal volume to the CMS material was similarly tested across the same pressure range and used to empirically determine a temperature correction applied to the sample data.

[0107] The results of the PCT measurements are summarized in FIG. 2. A maximum excess capacity of 2.3 wt% H<sub>2</sub> was achieved at a pressure of about 20 bar, which had minimal variation from adsorption/desorption cycles. The consistency of the excess capacity profiles indicated that sample activation had little effect on the measured excess capacity of the CMS sample.

[0108] The hydrogen storage kinetics of the CMS sample was essentially instantaneous, as indicated by the hydrogen storage rate in a representative aliquot shown in FIG. 3. Each aliquot reached equilibrium in about 5 minutes, and about twenty aliquots were used in total over a five-hour adsorption run.

[0109] The results of this experiment indicated that the CMS material had an excess capacity of 2.3 wt% at a relatively modest pressure of about 20 bar. Given the surface area of about 425 m<sup>2</sup>/g for the CMS sample, the hydrogen storage capacity of 2.3 wt% of H<sub>2</sub> was well above the storage capacity of 1 wt% of H<sub>2</sub> per 500 m<sup>2</sup>/g predicted by the Cahine rule thought to govern existing carbon-based hydrogen storage materials.

[0110] While the invention has been explained in relation to exemplary embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the description. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

**CLAIMS**

What is Claimed is:

1. A carbon molecular sieve comprising:
  - (a) an amount of carbon equal to or greater than about 99% by weight of the carbon molecular sieve;
  - (b) a plurality of micropore sidewalls forming interconnected micropores having internal diameters ranging from about 10 Å to about 20 Å, wherein the micropore sidewalls comprise from about 5% to about 40% of the total surface area of the carbon molecular sieve; and,
  - (c) a plurality of ultramicropore sidewalls forming interconnected ultramicropores having mean internal diameters ranging from about 3.0 Å to about 10 Å and individual internal diameters within about 0.5 Å of the mean internal diameter, wherein the ultramicropore sidewalls comprise from about 10% to about 60% of the total surface area of the carbon molecular sieve.
2. The carbon molecular sieve of claim 1, wherein the carbon molecular sieve selectively adsorbs at least one gas chosen from hydrogen, xenon, krypton, methane, ethane, carbon monoxide, carbon dioxide, or any combinations thereof.
3. A carbon molecular sieve comprising:
  - (a) an essentially spherical particle comprising carbon equal to or greater than about 99% by weight of the carbon molecular sieve, wherein the particle has a diameter ranging from about 2 μm to about 1000 μm;
  - (b) a plurality of micropore sidewalls forming interconnected micropores having internal diameters ranging from about 10 Å to about 20 Å, wherein the micropore sidewalls comprise from about 5% to about 40% of the total surface area of the carbon molecular sieve; and,
  - (c) a plurality of ultramicropore sidewalls forming ultramicropores having a mean internal diameter ranging from about 3 Å to about 7 Å and individual internal diameters within about 0.5 Å of the mean internal diameter, wherein the ultramicropore sidewalls comprise from about

10% to about 60% of the total surface area of the carbon molecular sieve.

4. The carbon molecular sieve of claim 3, wherein the carbon molecular sieve has a total surface area ranging from about 300 m<sup>2</sup>/g to about 3500 m<sup>2</sup>/g.
5. The carbon molecular sieve of claim 3, wherein the sieve has an excess hydrogen storage capacity ranging from about 1.5% to about 3.5% by weight of the sieve.
6. A method for forming a carbonaceous adsorbent, the method comprising:
  - (a) polysulfonating a microporous polymer ion exchange resin to produce a polysulfonated ion exchange resin; and,
  - (b) pyrolyzing the polysulfonated ion exchange resin to produce the carbonaceous adsorbent.
7. The method of claim 6, wherein the microporous polymer ion exchange resin is chosen from polymers of polyvinylidene monomers, polymers of monovinylidene monomers, polymers of monoethylenically unsaturated monomers, copolymers of polyvinylidene and monovinylidene monomers, copolymers of polyvinylidene and monoethylenically unsaturated monomers, copolymers of monovinylidene and monoethylenically unsaturated monomers, or any combination thereof.
8. The method of claim 6, wherein the microporous polymer ion exchange resin is polymerized divinylbenzene.
9. The method of claim 6, wherein the pyrolysis of the polysulfonated ion exchange resin is conducted at a temperature ranging from about 300° C to about 1300° C.
10. The method of claim 6 wherein the microporous polymer ion exchange resin is polysulfonated by contacting the resin with an amount of fuming sulfuric acid.
11. A method for forming a carbon molecular sieve, the method comprising:

- (a) polysulfonating a microporous polymer ion exchange resin to produce a polysulfonated ion exchange resin;
  - (b) pyrolyzing the polysulfonated ion exchange resin to produce the carbonaceous adsorbent;
  - (c) activating the carbonaceous adsorbent to form an activated carbonaceous adsorbent; and,
  - (d) pyrolyzing the activated carbonaceous adsorbent to form the carbon molecular sieve.
12. The method of claim 11, wherein the microporous polymer ion exchange resin is chosen from polymers of polyvinylidene monomers, polymers of monovinylidene monomers, polymers of monoethylenically unsaturated monomers, copolymers of polyvinylidene and monovinylidene monomers, copolymers of polyvinylidene and monoethylenically unsaturated monomers, copolymers of monovinylidene and monoethylenically unsaturated monomers, or any combination thereof.
13. The method of claim 11, wherein the microporous polymer ion exchange resin is polymerized divinylbenzene.
14. The method of claim 11, wherein the pyrolysis of the polysulfonated ion exchange resin is conducted at a temperature ranging from about 300° C to about 1300° C.
15. The method of claim 11, wherein the microporous polymer ion exchange resin is polysulfonated by contacting the resin with an amount of fuming sulfuric acid.
16. The method of claim 11, wherein the carbonaceous adsorbent is activated by contacting the adsorbent with a physical activation gas at a temperature ranging from about 300° C to about 1200° C.
17. The method of claim 16, wherein the physical activation gas is chosen from steam, oxygen, carbon dioxide, or any combination thereof.

18. The method of claim 11, wherein the pyrolysis of the carbonaceous adsorbent is conducted at a temperature ranging from about 900° C to about 1200° C.
19. A method for forming a carbon molecular sieve, the method comprising:
  - (a) contacting a porous polymer ion exchange resin with an amount of fuming sulfuric acid ranging from about 100% to about 2000% of the total weight of the ion exchange resin at a temperature ranging from about 100° C to about 180° C for a period ranging from about five hours to about 72 hours to form a polysulfonated ion exchange resin;
  - (b) pyrolyzing the polysulfonated ion exchange resin at a temperature ranging from about 300° C to about 1200° C for a period ranging from about 15 minutes to about two hours to form a carbonaceous adsorbent;
  - (c) contacting the carbonaceous adsorbent with a physical activation gas chosen from steam, oxygen, carbon dioxide, or any combination thereof, at a temperature ranging from about 500° C to about 1200° C to form an activated carbonaceous adsorbent; and,
  - (d) pyrolyzing the activated carbonaceous adsorbent at a temperature ranging from about 560° C to about 1300° C for a period of about 15 minutes to about two hours to form the carbon molecular sieve.
20. A method for storing an amount of molecular hydrogen gas comprising contacting the molecular hydrogen gas with a carbon molecular sieve at a pressure ranging from about 1 psig to about 1000 psig , wherein the carbon molecular sieve comprises:
  - (a) an essentially spherical particle comprising carbon equal to or greater than about 99% by weight of the particle, wherein the particle has a diameter ranging from about 2  $\mu\text{m}$  to about 1000  $\mu\text{m}$ ;
  - (b) a plurality of micropore sidewalls forming interconnected micropores having internal diameters ranging from about 10 Å to about 20 Å, wherein the micropore sidewalls comprise from about 5% to about 40% of the total surface area of the particle; and,
  - (c) a plurality of ultramicropore sidewalls forming ultramicropores having internal diameters ranging from about 4.5 Å to about 5.5 Å, wherein the

ultramicropore sidewalls comprise from about 10% to about 60% of the total surface area of the particle.

21. The method of claim 20, wherein the carbon molecular sieve particles have a maximum excess storage capacity ranging from about 1.5% to about 3.5% by weight of the particles.
22. A method for separating an amount of a molecular gas chosen from hydrogen, helium, xenon, krypton, methane, ethane, carbon monoxide, or carbon dioxide from a mixture of gases comprising the molecular gas, the method comprising contacting the mixture of gases with a carbon molecular sieve particle at a pressure ranging from about 1 psig to about 1000 psig, wherein the carbon molecular sieve particle comprises:
  - (a) an essentially spherical particle comprising carbon equal to or greater than about 99% by weight of the particle, wherein the particle has a diameter ranging from about 2  $\mu\text{m}$  to about 1000  $\mu\text{m}$ ;
  - (b) a plurality of micropore sidewalls forming interconnected micropores having internal diameters ranging from about 10  $\text{\AA}$  to about 20  $\text{\AA}$ , wherein the micropore sidewalls comprise from about 5% to about 40% of the total surface area of the particle; and,
  - (c) a plurality of ultramicropore sidewalls forming ultramicropores having internal diameters ranging from about 4.5  $\text{\AA}$  to about 5.5  $\text{\AA}$ , wherein the ultramicropore sidewalls comprise from about 10% to about 60% of the total surface area of the particle.

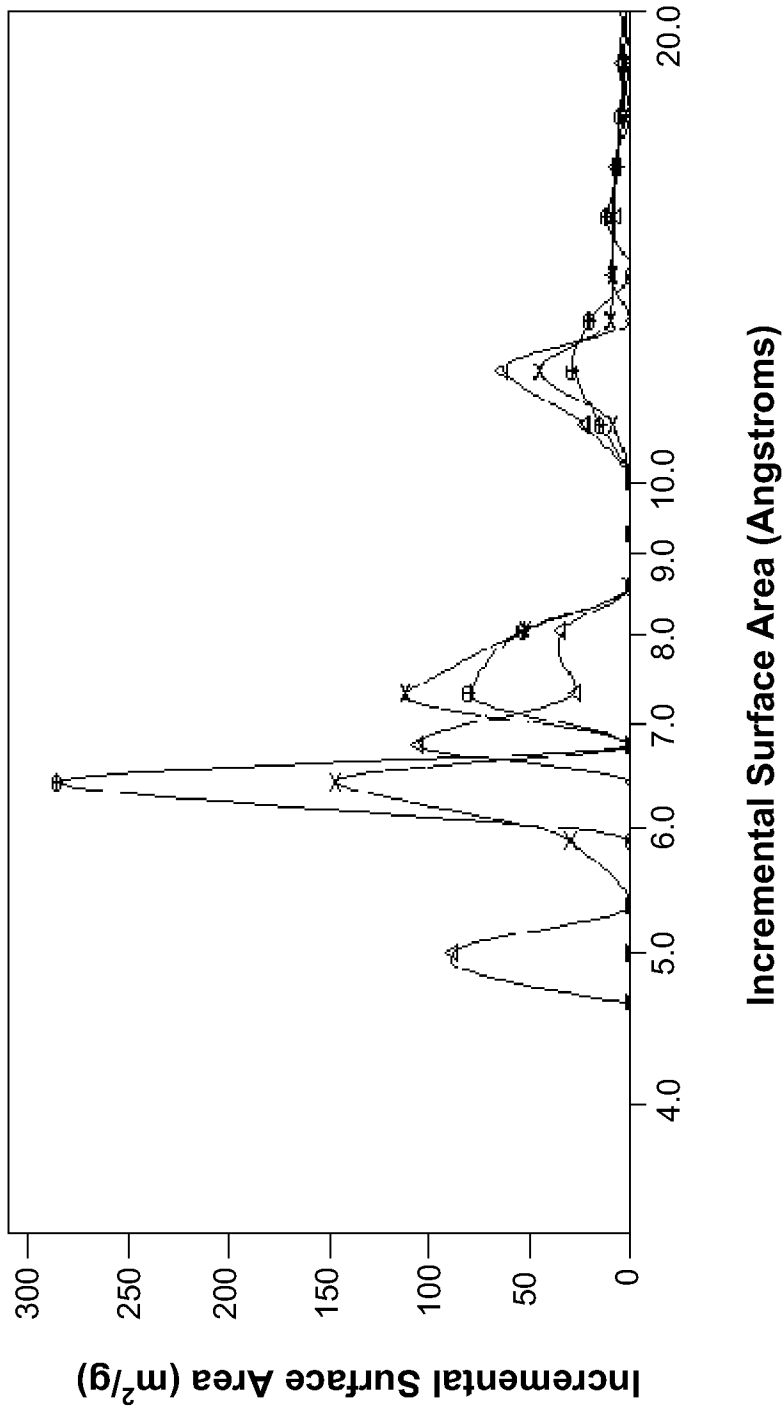


FIG. 1

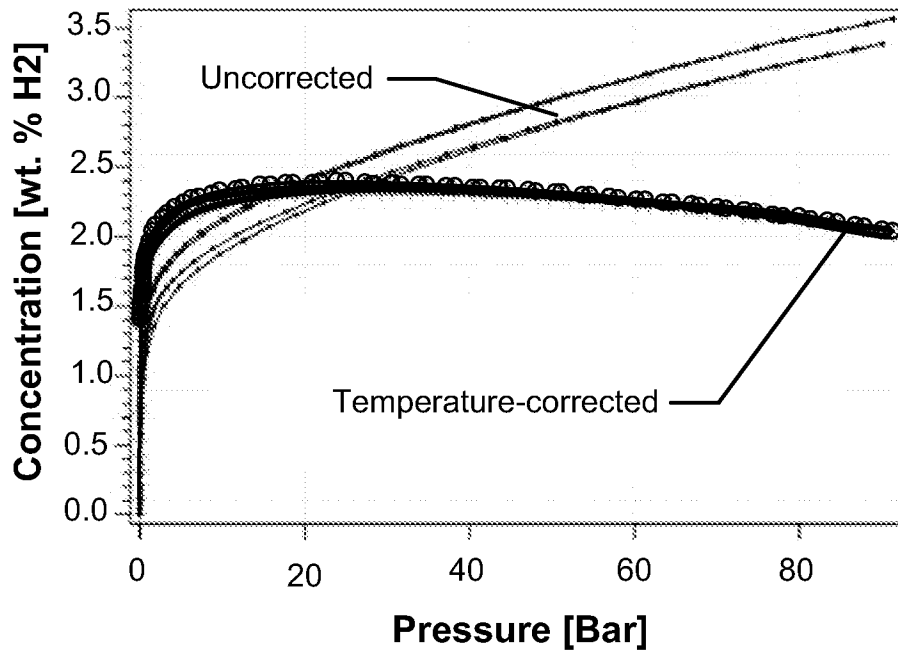


FIG. 2

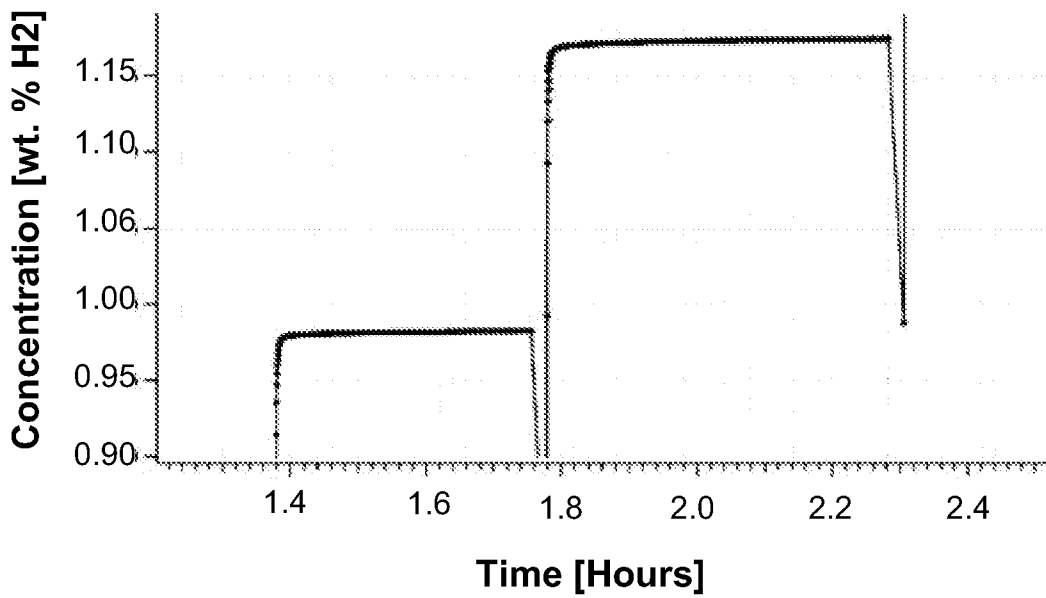


FIG. 3

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/20210

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(8) - C01B 31/08, C01B 31/10 (2011.01) USPC - 502/426,432 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC: C01B 31/08, C01B 31/10 (2011.01) USPC: 502/426,432 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC: 96/140,903; 502/416,418,423 (keyword limited; search terms below) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST(PGPB, USPT, EPAB, JPAB); Google Scholar; Google Patents Search terms: "molecular sieve" carbon "carbon molecular sieve" micropor\$8 ultramicropor\$8 "suspension polymerization" divinylbenzene extender\$2 hydrogen polysulfona\$8 sulfona\$8 polyvinylidene "ion exchange resin" adsor\$7 "surface area" pyrol\$7		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/0053284 A1 (Koros et al.) 09 May 2002 (09.05.2002), especially, para [0010], [0011], [0013], [0015], [0030], [0034], [0036], [0041]; [0099]	1-5, 11-22
Y	US 2009/0188392 A1 (Carruthers) 30 July 2009 (30.07.2009), especially, para [0042], [0045], [0066]; [0067]	1-5, 11-22
Y	US 5,104,425 A (Rao et al.) 14 April 1992 (14.04.1992), especially, col 2, ln 28-40; col 5, ln 46-49; col 9, ln 2-24; col 9, ln 36-39; col 9, ln 56-60	6-10, 12
Y	US 3,989,649 A (Kaiho et al.) 02 November 1976 (02.11.1976), especially, col 2, ln 28-40; col 3, ln 43-45; col 5, ln 50-53; col 5, ln 54-61	6-19
Y	US 2005/0032635 A1 (Yu et al.) 10 February 2005 (10.02.2005), especially, para [0014], [0039], [0056]	2-5, 20-22
Y	US 2002/0187896 A1 (Ryoo et al.) 25 October 2007 (25.10.2007), especially, para [0012], [0044]	20, 21
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/>		
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Date of the actual completion of the international search 15 February 2011 (15.02.2011)		Date of mailing of the international search report <b>07 MAR 2011</b>
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774