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(54) Title: SHAPED BODY CONTAINING POROUS AROMATIC FRAMEWORK (PAF) MATERIAL

(57) Abstract: The present invention relates to shaped bodies of compositions comprising a porous aromatic covalent framework polymer, wherein the polymer comprises at least one monomer unit, the at least one monomer unit comprising at least one aromatic ring and the at least one monomer unit having at least three binding sites to adjacent monomer units in the polymer and a core, wherein the at least three binding sites are located on at least one atom of the core and wherein the at least one atom is free of covalent bonds to hydrogen; and at least one binder additive. The invention also relates to methods for the preparation of said shaped bodies and their uses.

Shaped body containing Porous Aromatic Framework (PAF) material

Description

This patent application claims the benefit of pending US Provisional Patent Application Serial Number 61/493,529, filed June 6, 2011 incorporated in its entirety herein by reference.

The present invention relates to shaped bodies containing a porous aromatic framework, methods for their preparation and their use.

A new class of highly interesting porous aromatic covalent framework (PAF) polymers has been discovered recently, which can be compared with zeolites and MOF materials in terms of their porosity.

PAF polymers are characterized by a rigid framework mainly comprised of aromatic rings. The framework is usually built up by addition or substitution reaction of one or more monomers. Typical reactions are C-C coupling reactions or addition reactions under ring formation. PAF polymers typically show water and temperature resistant behavior.

PAF polymers are described by, e.g., T. Ben et al, *Angew. Chem. Int. Ed.* 48 (2009), 9457-9460; Z. Wang et al., *Chem. Commun.* 46 (2010), 7730-7732; J. Schmidt et al., *Macromolecules* 42 (2009), 4426-4429; M. Rose et al., *Chem. Commun.* 2008, 2462-2464; H. Ren et al., *Chem. Commun.* 46 (2010), 291-293; A. Trewin et al., *Angew. Chem. Int. Ed.* 49 (2010), 1533-1535; J. Holst et al., *Macromolecules* 43 (2010), 8531-8538; W. Lu et al., *Chem. Mater.* 22 (2010), 5464-5472 P. Pandey et al., *J. Mat. Chem.* 21 (2011), 1700-1703 and US 2010/0331436 A1.

However these PAF polymers are generally obtained as small crystallites or powders and thus cannot be used for potential applications like the storage of gases or as carriers in catalysis in an efficient way.

It is therefore an object of the present invention to provide PAF polymers in forms allowing a broad use of these applications.

The object is solved by a shaped body of a composition comprising

(a) a porous aromatic covalent framework polymer, wherein the polymer comprises at least one monomer unit, the at least one monomer unit comprising at least one aromatic ring and the at least one monomer unit having at least three binding sites to adjacent monomer units in the polymer and a core, wherein the at least three binding sites are located on at least one atom of the core and wherein the at least one atom is free of covalent bonds to hydrogen;

(b) at least one binder additive.

Surprisingly, it has been found that PAF powder can be converted into shaped bodies as described herein.

The term "shaped body" as used in the present invention thereby refers to shaped bodies obtained by molding processes and to shaped bodies obtained by applying the active material onto a (porous) substrate. The term "shaped body" will be defined further below.

As described above PAF polymers and their preparation are described in, for example, Z. Wang et al., *Chem. Commun.* 46 (2010), 7730-7732; J. Schmidt et al., *Macromolecules* 42 (2009), 4426-4429; M. Rose et al., *Chem. Commun.* 2008, 2462-2464; H. Ren et al., *Chem. Commun.* 46 (2010), 291-293; A. Trewin et al., *Angew. Chem. Int. Ed.* 49 (2010), 1533-1535; J. Holst et al., *Macromolecules* 43 (2010), 8531-8538; W. Lu et al., *Chem. Mater.* 22 (2010), 5464-5472 and US 2010/0331436 A1. The content of these publications and especially the PAF polymers disclosed therein, to which reference is made herein, is fully incorporated in the content of the present application.

The porous aromatic covalent framework polymer is characterized in that the polymer comprises at least one monomer unit (like one, two, three, or more - preferably, one or two), the at least one monomer unit comprising at least one aromatic ring and the at least one monomer unit having at least three binding sites to adjacent monomer units in the polymer and a core, wherein the at least three binding sites are located on at least one atom of the core and wherein the at least one atom is free of covalent bonds to hydrogen (to guarantee the desired rigidity).

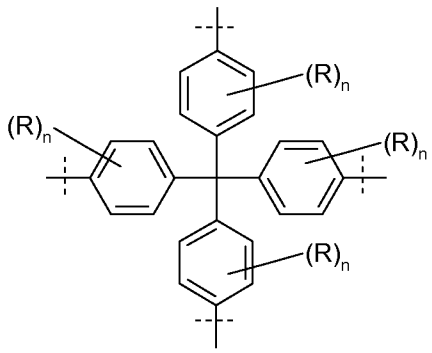
Accordingly, “aromatic” in the term “porous aromatic framework” indicates that the at least one monomer unit has to comprise at least one aromatic ring.

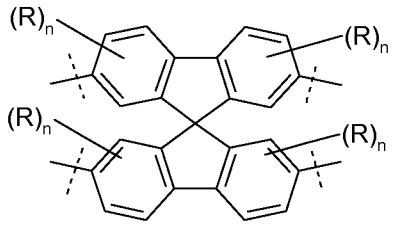
Preferably, the at least one monomer unit has four binding sites.

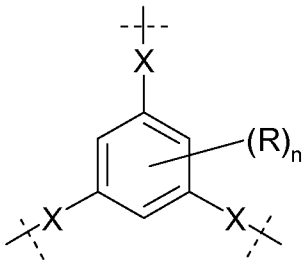
Preferably, the at least one aromatic ring is selected from the group consisting of benzene, naphthalene, biphenyl, pyridine, pyrimidine, pyridazine, pyrazine and triazine; more preferably, benzene, pyridine and triazine; even more preferably, benzene.

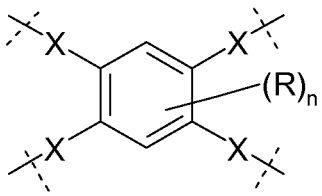
Preferably, the at least one atom of the core is a quaternary carbon atom.

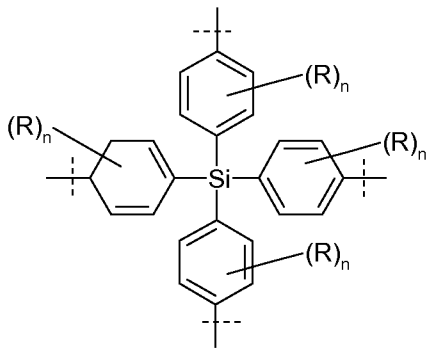
Preferably, the core of the at least one monomer unit is selected from the group consisting of

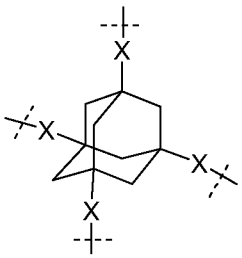












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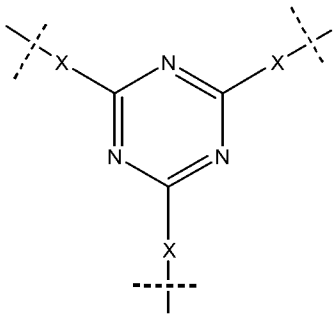

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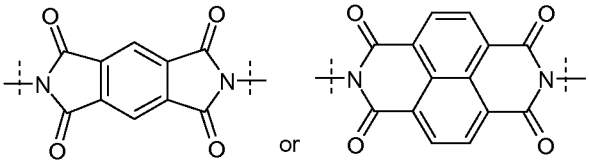
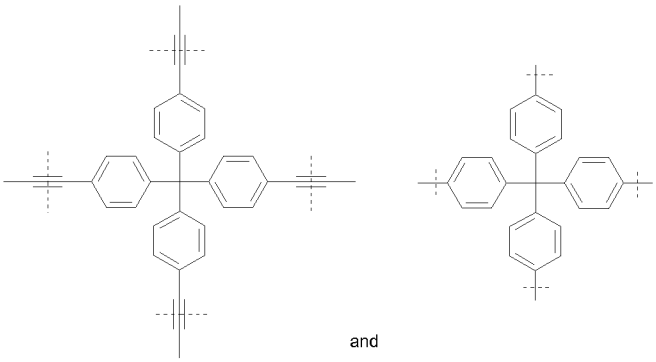
wherein n is an integer of 0, 1, 2, or 3 (preferably 0); each R is independently selected from the group consisting of R^1, NH_2, NHR^1, NR^1_2, C(O)OH, $C(O)OR^1$, OH, and OR^1; R^1 is methyl, or ethyl; X is phenylene, or -≡-, and the dotted lines indicate the binding sites.

Preferably, the polymer is a homo polymer. More preferably, the monomer unit of the homo polymer comprises a tetrakisphenylmethane, a tetrakisphenylsilane, or a 1,3,5,7-tetrakisphenyladamantane moiety; more preferably, a tetrakisphenylmethane moiety. Even more preferably, the homo polymer consists of these moieties, which are inter-connected by a covalent bond, -≡-, 1,2,3-triazole, 1,3,5-triazine,



or

In a preferred embodiment the homo polymer consists of a monomer unit selected from the group consisting of



and

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wherein the dotted lines indicate the attachment of the monomer unit to adjacent monomer units.

In addition, the shaped body of the present invention comprises at least one binder additive.

Suitable binders are described below. Preferably, the at least one binder is an oxygen containing binder. More preferably, the at least one binder is selected from the group consisting of an oxygen-containing aluminium compound, a silicium oxide and a silicium organic compound, like tetraethyl orthosilicate.

Such compounds care typically commercially available, like trade names Pural® SB, Ludox® AS 40, or Silres® MSE100.

Preferably, the amount of the porous aromatic covalent framework polymer based on the total weight of the shaped body is from 40 to 99 wt.-%.

Preferably, the amount of the at least one binder additive based on the total weight of the shaped body is from 1 to 60 wt.-%.

Preferably, the shaped body of the present invention has a cutting hardness of 0.5 N to 100 N. This is especially preferred for a shaped body that has a diameter of at least 1 mm and not more than 10 mm and a length of at least 1 mm and not more than 30 mm. Preferably, the cutting hardness is from 1.5 N to 30 N. This is especially preferred for a shaped body that has a diameter of at least 1 mm and not more than 5 mm and a length of at least 1 mm and not more than 25 mm, more preferred a diameter of at least 1 mm and not more than 4 mm and a length of at least 1 mm and not more than 20 mm, most preferred a diameter of at least 1 mm and not more than 3 mm and a length of at least 1 mm and not more than 15 mm.

The determination/measurement of the cutting hardness was carried out as described in the earlier German patent application no. 103261137.0 of June 6, 2003 (BASF AG): The cutting hardnesses were measured on an apparatus from Zwick (model: BZ2.5/TS1S; initial loading: 0.5 N, preliminary advance rate: 10 mm/min; test speed: 1.6 mm/min) and are the means of in each case 10 measured catalyst extrudates. In detail, the cutting hardness was determined as follows: Extrudates were loaded with increasing force by means of a cutter having a thickness of 0.3 mm until the extrudate had been cut through. The force required for this is the cutting hardness in N (Newton). The determination was carried out on a testing apparatus from Zwick, Ulm, having a rotating plate in a fixed position and a freely movable, vertical punch with built-in cutter having a thickness of 0.3 mm. The movable punch with the cutter was connected to a load cell to record the force and during the measurement moved towards the rotating plate on which the extrudate to be measured was located. The test apparatus was con-

trolled via a computer which recorded and evaluated the measurement results. 10 straight, preferably crack-free extrudates were taken from a well-mixed sample and their cutting hardnesses were determined and subsequently averaged.

In a preferred embodiment, the specific surface area of the shaped body of the present invention, as calculated according to the Langmuir model (DIN 66131, 66134) is above 50 m^2/g, further preferred above 100 m^2/g, more preferably above 150 m^2/g, particularly preferred above 500 m^2/g and may increase into the region above 3000 m^2/g.

The surface area per volume of the shaped bodies according to the present invention preferably amounts to 210 – 325 m^2/mL compared to 183 m^2/mL for the PAF powder. The preferred ratio of the surface area per volume of the shaped bodies to the surface area per volume of the PAF powder is 1.1 to 1.8. The values obtained for the surface area were obtained according to the Langmuir model. The surface area per volume was determined by applying the bulk density of the PAF powder and the shaped bodies respectively.

Another aspect of the present invention is a method for preparing a shaped body of the present invention comprising the steps of

(a) mixing a composition comprising the porous aromatic covalent framework polymer as defined herein and the at least one binder additive as defined herein; and

(b) molding the composition into a shaped body.

Preferably, the molding comprises an extrusion step.

For the step of preparing shaped bodies containing PAF material, all processes of molding a powder and/or crystallites that are known to the expert are conceivable. Also, all processes of applying PAF material onto a substrate are conceivable. Preparing shaped bodies by a process involving molding is described first, followed by a description of the process of applying said material onto a (porous) substrate.

In the context of the present invention, the term "molding" refers to any process known to the expert in the field by which a substance that does not fulfill the above-mentioned requirement of a shaped body, i.e. any powder, powdery substance, array of crystallites etc., can be formed into a shaped body that is stable under the conditions of its intended use.

While the step of molding is mandatory, the following steps are optional according to the present invention:

(I) the molding may be preceded by a step of preparing a paste-like mass or a fluid containing the PAF material and the binder, for example by adding solvents or other additional substances,

(II) the molding may be followed by a step of finishing, in particular a step of drying, activating or impregnating.

The mandatory step of molding may be achieved by any method known to the expert to achieve agglomeration of a powder, a suspension or a paste-like mass. Such methods are described, for example, in *Ullmann's Enzyklopädie der Technischen Chemie*, 4th Edition, Vol. 2, p. 313 et seq., 1972, whose respective content is incorporated into the present application by reference.

In general, the following main pathways can be discerned: (i) briquetting, i.e. mechanical pressing of the powdery material, with or without binders and/or other additives, (ii) granulating (pelletizing), i.e. compacting of moistened powdery materials by subjecting it to rotating movements, and (iii) sintering, i.e. subjecting the material to be compacted to a thermal treatment. The latter is somewhat limited for the PAF material according to the invention due to the limited temperature stability of the organic materials.

Specifically, the molding step according to the invention is preferably performed by using at least one method selected from the following group: briquetting by piston presses, briquetting by roller pressing, briquetting with binders, pelletizing, compounding, melting, extruding, co-extruding, spinning, deposition, foaming, spray drying, coating, granulating, in particular spray granulating or granulating according to any process known within the processing of plastics or any combination of at least two of the aforementioned methods.

The preferred processes of molding are those in which the molding is affected by extrusion in conventional extruders, for example such that result in extrudates having a diameter of, usually, from about 1 to about 10 mm, in particular from about 1 to about 5 mm. Such extrusion apparatuses are described, for example, in *Ullmann's Enzyklopädie der Technischen Chemie*, 4th Edition, Vol. 2, p. 295 et seq., 1972. In addition to the use of an extruder, an extrusion press is preferably also used for molding.

The molding can be performed at elevated pressure (ranging from atmospheric pressure to several 100 bar), at elevated temperatures (ranging from room temperature to

300 °C) or in a protective atmosphere (noble gases, nitrogen or mixtures thereof). Any combinations of these conditions are possible as well.

The step of molding is performed in the presence of at least one binder and optional other additional substances that stabilize the materials to be agglomerated. As to the at least one binder, any material known to the expert to promote adhesion between the particles to be molded together can be employed. A binder, an organic viscosity-enhancing compound and/or a liquid for converting the material into a paste can be added to the PAF material, with the mixture being subsequently compacted in a mixing or kneading apparatus or an extruder. The resulting plastic material can then be molded, in particular using an extrusion press or an extruder, and the resulting moldings can then be subjected to the optional step (II) of finishing, for example drying, activating or impregnating.

A number of compounds can be used as binders. For example, according to US-A 5,430,000, titanium dioxide or hydrated titanium dioxide is used as the binder. Examples of further prior art binders are:

hydrated alumina or other aluminum-containing binders (WO 94/29408);
mixtures of silicon and aluminum compounds (WO 94/13584);
silicon compounds (EP-A 0 592 050);
clay minerals (JP-A 03 037 156);
alkoxysilanes (EP-B 0 102 544);
amphiphilic substances.

Other conceivable binders are in principle all compounds used to date for the purpose of achieving adhesion in powdery materials. Compounds, in particular oxygen-containing, of silicon, of aluminum, of boron, of phosphorus, of zirconium and/or of titanium are preferably used. Of particular interest as a binder are alumina, silica, where the SiO_2 may be introduced into the shaping step as a silica sol or in the form of tetraalkoxysilanes, and silicones. Oxides of magnesium and of beryllium and clays, for example montmorillonites, kaolins, bentonites, halloysites, dickites, nacrites and anauxites, may furthermore be used as binders. Tetraalkoxysilanes are particularly used as binders in the present invention. Specific examples are tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane and tetrabutoxysilane, the analogous tetraalkoxytitanium and tetraalkoxyzirconium compounds and trimethoxy-, triethoxy-, tripropoxy- and tributoxyaluminum, tetramethoxysilane and tetraethoxysilane being particularly preferred.

In addition, organic viscosity-enhancing substances and/or hydrophilic polymers, e.g. cellulose or polyacrylates may be used. The organic viscosity-enhancing substance

used may likewise be any substance suitable for this purpose. Those preferred are in particular hydrophilic polymers, e.g., cellulose, starch, polyacrylates, polymethacrylates, polyvinyl alcohol, polyvinylpyrrolidone, polyisobutene and polytetrahydrofuran. These substances primarily promote the formation of a plastic material during the kneading, molding and drying step by bridging the primary particles and moreover ensuring the mechanical stability of the molding during the molding and the optional drying process.

There are no restrictions at all with regard to the optional liquid which may be used to create a paste-like substance, either for the optional step (I) of mixing or for the mandatory step of molding. In addition to water, alcohols may be used, provided that they are water-miscible. Accordingly, both monoalcohols of 1 to 4 carbon atoms and water-miscible polyhydric alcohols may be used. In particular, methanol, ethanol, propanol, n-butanol, isobutanol, tert-butanol and mixtures of two or more thereof are used. However toluene is also suitable.

Amines or amine-like compounds, for example tetraalkylammonium compounds or aminoalcohols, and carbonate-containing substances, such as calcium carbonate, may be used as further additives. Such further additives are described in EP-A 0 389 041, EP-A 0 200 260 and WO 95/19222, which are incorporated fully by reference in the context of the present application.

Most, if not all, of the additive substances mentioned above may be removed from the shaped bodies by drying or heating, optionally in a protective atmosphere or under vacuum. In order to keep the PAF material intact, the shaped bodies are preferably not exposed to temperatures exceeding 300 °C. However, studies show that heating/drying under the aforementioned mild conditions, in particular drying in vacuo, preferably well below 300 °C is sufficient to at least remove organic compounds and water out of the pores of the PAF material. Generally, the conditions are adapted and chosen depending upon the additive substances used.

In general it is possible either to add first the binder, then, for example, the PAF material and, if required, the additive and finally the mixture containing at least one alcohol and/or water or to interchange the order with respect to any of the aforementioned components.

As far as the step of mixing is concerned, for example, of the material containing a PAF material and a binder and optionally further process materials (= additional materials), all methods known to the expert in the fields of materials processing and unit opera-

tions can be used. If the mixing occurs in the liquid phase, stirring is preferred, if the mass to be mixed is paste-like, kneading and/or extruding are preferred and if the components to be mixed are all in a solid, powdery state, mixing is preferred. The use of atomizers, sprayers, diffusers or nebulizers is conceivable as well if the state of the components to be used allows the use thereof. For paste-like and powder-like materials the use of static mixers, planetary mixers, mixers with rotating containers, pan mixers, pug mills, shearing-disk mixers, centrifugal mixers, sand mills, trough kneaders, internal mixers, and continuous kneaders are preferred. It is explicitly included that a process of mixing may be sufficient to achieve the molding, i.e., that the steps of mixing and molding coincide.

The present invention further provides for the use of a shaped body according to the invention for the uptake of at least one substance for the purposes of its storage, separation, controlled release, chemical reaction or as support.

Accordingly, a further aspect of the present invention is a method of storing, separating, controlled releasing, for carrying out a chemical reaction or for preparing a support, the method comprising the step of contacting the shaped body of the present invention with at least one substance.

The at least one substance is preferably a gas or a gas mixture. Liquids and metals are also possible.

Processes for storage by means of shaped bodies according to the present invention can be used as known for shaped bodies of metal organic frameworks. In general these are described in WO-A 2005/003622, WO-A 2003/064030, WO-A 2005/049484, WO-A 2006/089908 and DE-A 10 2005 012 087. Preferred gases for storage are methane, methane containing gas mixtures, like natural gas, shale gas or town gas, and hydrogen.

Processes for separation or purification by means of shaped bodies according to the present invention can be used as known for shaped bodies of metal organic frameworks. In general these are described in EP-A 1 674 555, DE-A 10 2005 000938 and DE-A 10 2005 022 844. A gas which is preferably separated off is carbon dioxide, in particular from a gas mixture which further comprises carbon monoxide.

If the shaped bodies of the invention are used for storage, this is preferably carried out in a temperature range from -200°C to +80°C. A temperature range from -80°C to

+80°C is more preferred. A preferred pressure range is from 1 bar to 200 bar (absolute), in particular from 2 bar to 100 bar.

For the purposes of the present invention, the terms "gas" and "liquid" are used in the interests of simplicity, but gas mixtures and liquid mixtures or liquid solutions are likewise encompassed by the term "gas" or "liquid".

Preferred gases are hydrogen, natural gas, town gas, hydrocarbons, in particular methane, ethane, ethene, acetylene, propane, propene, n-butane and i-butane, 1-butene, 2-butene, carbon monoxide, carbon dioxide, nitrogen oxides, oxygen, sulfur oxides, halogens, halogenated hydrocarbons, NF_3, SF_6, ammonia, hydrogen sulfide, ammonia, formaldehyde, noble gases, in particular helium, neon, argon, krypton and xenon.

Particular preference is given to the use of the framework of the invention for the storage of a gas at a minimum pressure of 1 bar (absolute). The minimum pressure is more preferably 3 bar (absolute), in particular 10 bar (absolute). The gas is in this case particularly preferably hydrogen, methane or a methane containing gas, like natural gas, shale gas or town gas.

The gas is particularly preferably carbon dioxide which is separated off from a gas mixture comprising carbon dioxide. The gas mixture preferably comprises carbon dioxide together with at least H_2, CH_4 or carbon monoxide. In particular, the gas mixture comprises carbon monoxide in addition to carbon dioxide. Very particular preference is given to mixtures which comprise at least 10 and not more than 45% by volume of carbon dioxide and at least 30 and not more than 90% by volume of carbon monoxide.

A preferred embodiment is pressure swing adsorption using a plurality of parallel adsorber reactors, with the adsorbent bed being made up completely or partly of the material according to the invention. The adsorption phase for the CO_2/CO separation preferably takes place at CO_2 partial pressure of from 0.6 to 3 bar and a temperature of at least 20°C, but not more than 70°C. To desorb the adsorbed carbon dioxide, the total pressure in the adsorber reactor concerned is usually reduced to values in the range from 100 mbar to 1 bar.

However, the at least one substance can also be a liquid. Examples of such a liquid are disinfectants, inorganic or organic solvents, fuels, in particular gasoline or diesel, hydraulic fluid, radiator fluid, brake fluid or an oil, in particular machine oil. The liquid can also be halogenated aliphatic or aromatic, cyclic or acyclic hydrocarbons or mixtures thereof. In particular, the liquid can be acetone, acetonitrile, aniline, anisol, benzene,

benzonitrile, bromobenzene, butanol, tert-butanol, quinoline, chlorobenzene, chloroform, cyclohexane, diethylene glycol, diethyl ether, dimethylacetamide, dimethylformamide, dimethyl sulfoxide, dioxane, glacial acetic acid, acetic anhydride, ethyl acetate, ethanol, ethylene carbonate, ethylene dichloride, ethylene glycol, ethylene glycol dimethyl ether, formamide, hexane, isopropanol, methanol, methoxypropanol, 3-methyl-1-butanol, methylene chloride, methyl ethyl ketone, N-methylformamide, N-methylpyrrolidone, nitrobenzene, nitromethane, piperidine, propanol, propylene carbonate, pyridine, carbon disulfide, sulfolane, tetrachloroethene, carbon tetrachloride, tetrahydrofuran, toluene, 1,1,1-trichloroethane, trichloroethylene, triethylamine, triethylene glycol, triglyme, water or mixtures thereof.

Furthermore, the at least one substance can be an odorous substance.

The odorous substance is preferably a volatile organic or inorganic compound which comprises at least one of the elements nitrogen, phosphorus, oxygen, sulfur, fluorine, chlorine, bromine or iodine or is an unsaturated or aromatic hydrocarbon or a saturated or unsaturated aldehyde or a ketone. More preferred elements are nitrogen, oxygen, phosphorus, sulfur, chlorine, bromine; and particular preference is given to nitrogen, oxygen, phosphorus and sulfur.

In particular, the odorous substance is ammonia, hydrogen sulfide, sulfur oxides, nitrogen oxides, ozone, cyclic or acyclic amines, thiols, thioethers and aldehydes, ketones, esters, ethers, acids or alcohols. Particular preference is given to ammonia, hydrogen sulfide, organic acids (preferably acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, caproic acid, heptanoic acid, lauric acid, pelargonic acid) and cyclic or acyclic hydrocarbons comprising nitrogen or sulfur and saturated or unsaturated aldehydes such as hexanal, heptanal, octanal, nonanal, decanal, octenal or nonenal and in particular volatile aldehydes such as butyraldehyde, propionaldehyde, acetaldehyde and formaldehyde and also fuels such as gasoline, diesel (constituents).

The odorous substances can also be fragrances which are used, for example, for producing perfumes. Examples of fragrances or oils which can release such fragrances are: essential oils, basil oil, geranium oil, mint oil, cananga oil, cardamom oil, lavender oil, peppermint oil, nutmeg oil, camomile oil, eucalyptus oil, Rosemary oil, lemon oil, lime oil, orange oil, bergamot oil, muscatel sage oil, coriander oil, cypress oil, 1,1-dimethoxy-2-phenylethane, 2,4-dimethyl-4-phenyltetrahydrofuran, dimethyltetrahydrobenzaldehyde, 2,6-dimethyl-7-octen-2-ol, 1,2-diethoxy-3,7-dimethyl-2,6-octadiene, phenylacetaldehyde, rose oxide, ethyl 2-methylpentanoate, 1-(2,6,6-trimethyl-1,3-

cyclohexadien-1-yl)-2-buten-1-one, ethyl vanillin, 2,6-dimethyl-2-octenol, 3,7-dimethyl-2-octenol, tert-butylcyclohexyl acetate, anisyl acetate, allyl cyclohexyloxyacetate, ethyl-linalool, eugenol, coumarin, ethyl acetoacetate, 4-phenyl-2,4,6-trimethyl-1,3-dioxane, 4-methylene-3,5,6,6-tetramethyl-2-heptanone, ethyl tetrahydrosafranate, geranyl nitrile, cis-3-hexen-1-ol, cis-3-hexenyl acetate, cis-3-hexenyl methyl carbonate, 2,6-dimethyl-5-hepten-1-al, 4-(tricyclo[5.2.1.0]decylidene)-8-butanal, 5-(2,2,3-trimethyl-3-cyclopentenyl)-3-methylpentan-2-ol, p-tert-butyl-alpha-methylhydrocinnamaldehyde, ethyl[5.2.1.0]tricyclodecanecarboxylate, geraniol, citronellol, citral, linalool, linalyl acetate, ionone, phenylethanol and mixtures thereof.

For the purposes of the present invention, a volatile odorous substance preferably has a boiling point or boiling point range below 300°C. The odorous substance is more preferably a readily volatile compound or mixture. In particular, the odorous substance has a boiling point or boiling range below 250°C, more preferably below 230°C, particularly preferably below 200°C.

Preference is likewise given to odorous substances which have a high volatility. The vapor pressure can be employed as a measure of the volatility. For the purposes of the present invention, a volatile odorous substance preferably has a vapor pressure of more than 0.001 kPa (20°C). The odorous substance is more preferably a readily volatile compound or mixture. The odorous substance particularly preferably has a vapor pressure of more than 0.01 kPa (20°C), more preferably a vapor pressure of more than 0.05 kPa (20°C). Particular preference is given to the odorous substances having a vapor pressure of more than 0.1 kPa (20°C).

In addition, the shaped bodies of the invention can be used as support, in particular as support of a catalyst.

Examples

The following examples show different approaches to prepare shaped bodies from PAF material. The powder of the PAF material used was prepared according to T. Ben et al, *Angew. Chem. Int. Ed.* 48 (2009), 9457-9460 and exhibited the following properties: N_2 surface area: 2859 m²/g according to Langmuir; bulk density: 0.064 g/mL; skeletal density: 1,17 g/mL; water adsorption: 0.1-0.4% by weight at relative humidity of 10-80%.

The determination/measurement of the cutting hardness was carried out as described in the earlier German patent application no. 103261137.0 of June 6, 2003 (BASF AG): The cutting hardnesses were measured on an apparatus from Zwick (model: BZ2.5/TS1S; initial loading: 0.5 N, preliminary advance rate: 10 mm/min; test speed: 1.6 mm/min) and are the means of in each case 10 measured catalyst extrudates. In detail, the cutting hardness was determined as follows: Extrudates were loaded with increasing force by means of a cutter having a thickness of 0.3 mm until the extrudate had been cut through. The force required for this is the cutting hardness in N (Newton). The determination was carried out on a testing apparatus from Zwick, Ulm, having a rotating plate in a fixed position and a freely movable, vertical punch with built-in cutter having a thickness of 0.3 mm. The movable punch with the cutter was connected to a load cell to record the force and during the measurement moved towards the rotating plate on which the extrudate to be measured was located. The test apparatus was controlled via a computer which recorded and evaluated the measurement results. 10 straight, preferably crack-free extrudates were taken from a well-mixed sample and their cutting hardnesses were determined and subsequently averaged.

Example 1:

Extruding shaped bodies of PAF material using Silres® MSE100

According to the invention, 1.6 g of PAF material were kneaded with 0.1 g of methylcellulose at room temperature for 5 minutes. 0.6 to 1.0 g of Silres® MSE100 (methylsilicone, 70% by weight solution in toluene) was added and the mixture was kneaded for 5 minutes. The mixture was densified with 13.5 mL of water using a mortar. The paste was placed in a ram extruder and extruded to form 2.0 mm extrudates. The extrudates were dried at 120 °C in a drying oven for 23 h. The cutting hardness of the shaped bodies was 2.5 N, the N_2 surface area was 1617 m²/g according to Langmuir. The bulk density amounted to 0,13 g/mL.

Example 2:

Extruding shaped bodies of PAF material using Ludox® AS 40

According to the invention, 1.0 g of PAF material was kneaded with 0.09 g of methylcellulose at room temperature for 2 minutes. 0.6 g of Ludox® AS 40 (colloidal silica, 39.5% by weight solution in ammoniacal water) and two portions 5.0 and 3.0 mL of water were added and the mixture was densified for 5 minutes after each addition. The

paste was placed in a ram extruder and extruded to form 2.0 mm extrudates. The extrudates were dried at 120 °C in a drying oven for 23 h. The cutting hardness of the shaped bodies was 3.3 N, the N_2 surface area was 2029 m²/g according to Langmuir and the bulk density amounted to 0,14 g/mL.

Example 3:

Extruding shaped bodies of PAF material using Pural® SB

According to the invention, 1.0 g of PAF material was kneaded with 0.33 g of Pural® SB at room temperature for 2 minutes. A solution of 0.01 g of formic acid in 2.0 mL of water was added and the mixture was densified for 5 minutes. 6.0 mL of water were added and the mixture was densified for 5 minutes. The paste was placed in a ram extruder and extruded to form 2.0 mm extrudates. The extrudates were dried at 120 °C in a drying oven for 23 h. The cutting hardness of the shaped bodies was 3.8 N, the N_2 surface area was 2323 m²/g according to Langmuir and the bulk density amounted to 0,14 g/mL.

Example 4:

Extruding shaped bodies of PAF material using tetraethyl orthosilicate

According to the invention, 1.0 g of PAF material was kneaded with 0.09 g of methylcellulose at room temperature for 2 minutes. 0.9 g of tetraethyl orthosilicate and two portions (3.0 mL each) of water were added and the mixture was densified for 5 minutes after each addition. The paste was placed in a ram extruder and extruded to form 2.0 mm extrudates. The extrudates were dried at 120 °C in a drying oven for 23 h. The cutting hardness of the shaped bodies was 8.3 N, the N_2 surface area was 1806 m²/g according to Langmuir and the bulk density amounted to 0,18 g/mL.

Shaped body containing Porous Aromatic Framework (PAF) material

Claims

1. A shaped body of a composition comprising

   (a) a porous aromatic covalent framework polymer, wherein the polymer comprises at least one monomer unit, the at least one monomer unit comprising at least one aromatic ring and the at least one monomer unit having at least three binding sites to adjacent monomer units in the polymer and a core, wherein the at least three binding sites are located on at least one atom of the core and wherein the at least one atom is free of covalent bonds to hydrogen;

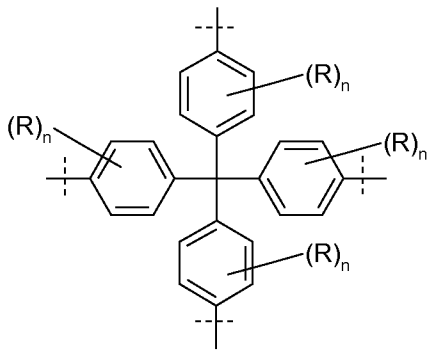
   (b) at least one binder additive.

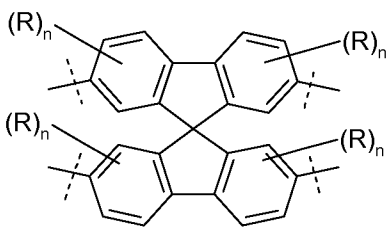
2. The shaped body of claim 1, wherein the at least one monomer unit has four binding sites.

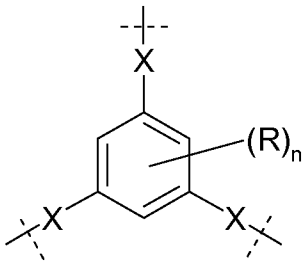
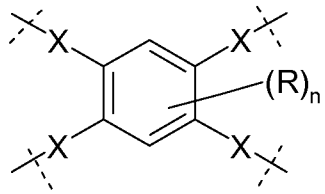
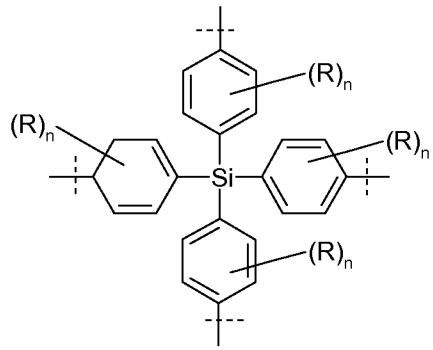
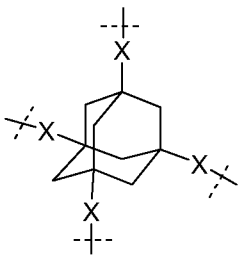
3. The shaped body of claim 1 or 2, wherein the at least one aromatic ring is selected from the group consisting of benzene, naphthalene, biphenyl, pyridine, pyrimidine, pyridazine, pyrazine and triazine.

4. The shaped body of any one of claims 1 to 3, wherein the at least one atom of the core is a quaternary carbon atom.

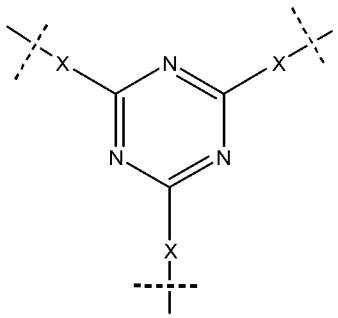
5. The shaped body of any one of claims 1 to 4, wherein the core of the at least one monomer unit is selected from the group consisting of





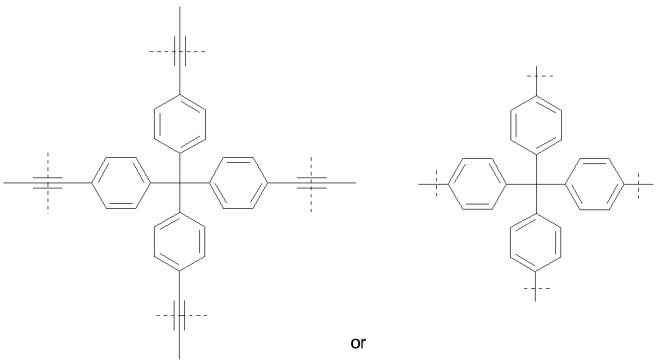
and



wherein n is an integer of 0, 1, 2, or 3; each R is independently selected from the group consisting of R^1, NH_2, NHR^1, NR^1_2, C(O)OH, $C(O)OR^1$, OH, and OR^1; R^1 is methyl, or ethyl; X is a phenylene or -≡-, and the dotted lines indicate the binding sites.

6. The shaped body of any one of claims 1 to 5, wherein the polymer is a homo polymer.

7. The shaped body of claim 6, wherein the homopolymer consists of a monomer unit



8. The shaped body of any one of claims 1 to 7, wherein the at least one binder is an oxygen containing binder.

9. The shaped body of any one of claims 1 to 8, wherein the at least one binder is selected from the group consisting of an oxygen-containing aluminum compound, a silicium oxide and a silicium organic compound.

10. The shaped body of any one of claims 1 to 9, wherein the at least one binder is selected from Pural® SB, Ludox® AS 40, Silres® MSE100, tetraethyl orthosilicate.

11. The shaped body of any one of claims 1 to 10, wherein the amount of the porous aromatic covalent framework polymer based on the total weight of the shaped body is from 40 to 99 wt.-%.

12. The shaped body of any one of claims 1 to 11, wherein the amount of the at least one binder additive based on the total weight of the shaped body is from 1 to 60 wt.-%.

13. A method for preparing a shaped body of any one of claims 1 to 12 comprising the steps of

(a) mixing a composition comprising the porous aromatic covalent framework polymer as defined in any one of claims 1 to 10 and the at least one binder additive as defined in any one of claims 1 to 10; and
(b) molding the composition into a shaped body.

14. The method of claim 13, wherein the molding comprises an extrusion step.

15. Use of a shaped body of any one of claims 1 to 12 for the uptake of at least one substance for the purposes of its storage, separation, controlled release, chemical reaction or as support.

16. The use of claim 15, wherein the at least one substance is a gas or gas mixture.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2012/051966

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC:B01J20/-, C08K3/-

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)

CNPAT; DWPI; SIPOABS

Porous, polymer, binder, alumina, aluminum, silicium, silicon, alkoxysilane?, covalent, organic, framework, storage, separat+, release

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US2006185388A1(BASF AG etc.), 24 Aug.2006(24.08.2006), paragraphs [0001][0009][0010] [0023] [0080]-[0085][0088][0093]-[0095] in description	1-16
Y	US2010331436A1(BEN T etc.), 30 Dec.2010(30.12.2010), paragraphs [0004][0006] [0008]-[0009][0141] in description	1-16
Y	WO2005049484A1(BASF AG), 02 Jun.2005(02.06.2005), claims 1-17	1-16
Y	US2004265670A1(BASF AG etc.), 30 Dec.2004(30.12.2004), claims 1-34, paragraphs [0086]-[0094] in description	1-16
A	US2007209505A1 (UOP LLC etc.), 13 Sep.2007(13.09.2007), the whole document	1-16

☐ Further documents are listed in the continuation of Box C. ☒ 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

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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
28 Aug.2012(28.08.2012)	**13 Sep. 2012 (13.09.2012)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer BAI Yu Telephone No. (86-10)62084467

Form PCT/ISA /210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2012/051966

(1)Continue of CLASSIFICATION OF SUBJECT MATTER

B01J20/26 (2006.01) i

C08K3/22 (2006.01) i

C08K3/34 (2006.01) i

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

(2)Continue of Information on patent family members

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
		WO2007106677A2	20.09.2007

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2012/051966

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