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(54) Title: STABLE SPHERICAL, POROUS METAL-ORGANIC FRAMEWORK SHAPED BODIES FOR GAS STORAGE AND GAS SEPARATION

(57) Abstract: The present invention relates to a method for preparing a MOF shaped body in the form of spheres, MOF shaped bodies in the form of spheres and the use of MOF shaped bodies in the form of spheres.



WO 2014/118054 A1

Stable spherical, porous metal-organic framework shaped bodies for gas storage and gas separation

Description

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Due to their large surface areas of up to 10 000 m²/g, metal-organic framework (MOF) materials are of interest for applications in gas storage or gas separation. For most applications, it is necessary to process the pulverulent materials to compact shaped bodies. These can be handled more conveniently and especially in a safer manner, allow better exploitation of the apparatus or tank volumes and prevent large pressure drops. Prerequisites for the successful use of such shaped bodies are, however, the absorption capacity and selectivity thereof, adequate thermal and mechanical stability and high abrasion resistance. Even the recurrent thermal shocks resulting from the heat of adsorption released in the course of continuous adsorption/desorption cycles can be sufficient in the case of the related zeolite shaped bodies to cause fracture and splintering of the bodies (DE 1 905 019). Mechanical stability is therefore indispensable particularly for MOF shaped bodies which are used in vehicle tanks exposed constantly to agitation.

The chemical and/or physical mechanisms in the course of compaction and setting of metal-organic framework materials are not nearly as well understood as is the case for the related class of the zeolites, and so the results which are achieved with new additives and shaped bodies can be predicted only with low certainty.

Spheres have particularly high stability since curve shapes distribute pressure exerted and thus withstand relatively high forces (cf. egg). As a result of the lack of edges as occur, for example, in the case of extrudates or tablets, the risk that material parts will splinter off under mechanical stress on the spheres is minimized.

The production of MOF tablets and extrudates has been described in WO 2003/102000 and WO 2006/050898.

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The use of MOF spheres of Cu-BTC (diameter 2-3 mm) has been described in a publication by M.G. Plaza et al. in Separation and Purification Technology 90 (2012) 109-119 for the separation of propane and propene. The publication refers to the production of the Cu-BTC powder. However, there is no explanation as to the manner in which the Cu-BTC spheres were produced. Nor is there any reference to other sources in which the sphere preparation is described.

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Chem. Commun. 48 (2012) 9388-9390 discloses core-shell spheres which are formed by using ca. 3 µm mesoporous silica spheres as the core onto which a shell of zeolite imidazolate frameworks, so-called ZIF-8 is grown.

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In Nature Chemistry 3 (2011) 347-348 the formation of hollow spheres is described.

WO2012/156436 describes the formation of MOF spheres by a gelation process from a MOF-gel precursor solution. The use of a binder is minimized in order to avoid blocking of the pores and the respective effects, e.g. decreasing specific surface and pore volume. The resulting MOF particles are obtained in the form of a dried gel (xerogel or aerogel).

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Typical processes in the state of the art for producing shaped bodies include extrusion, tabletting, kneading, pan milling and shaping. In the production of shaped bodies, it is possible to add further materials such as binders, lubricants or other additives which are added during the production process. It is likewise conceivable for the framework to comprise further constituents, for example adsorbents such as activated carbon or the like. Kneading and/or

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pan milling and shaping can be carried out by any suitable method, for example as described in Ullmanns Enzyklopädie der Technischen Chemie, 4th edition, Volume 2, p. 313 ff. (1972).

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It was the aim of the invention to provide mechanically stable, spheroidal MOF shaped bodies with high surface areas and high adsorption capacities. These can be used in gas storage and/or gas separation and can be produced via an industrially implementable, favorable production process. Preferred applications are the storage and/or separation of natural gas or shale gas, even more preferred is the storage of natural gas or shale gas in vehicle tanks.

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Established industrial processes for the production of spherical bodies of porous materials (namely zeolites and molecular sieves) are based on the use of intensive mixers, granulating pans, ballformers or marumerizers and binder additives. It has been found that, surprisingly, typical binders as used for the inorganic zeolites (e.g. kaolin, attapulgite, bentonite, palygorskite, montmorillonite, sepiolite, silicates and mixtures thereof, described, inter alia, in US 2 973 327, EP 0 940 174 and EP 1 468 731) also interact well with the semiorganic MOFs and lead to stable shaped bodies of appropriate hardness. Experts in the field expect that a switch to at least partly organic binders will be necessary, these having similar polarities to MOF frameworks and similar structures to the organic linkers thereof.

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The hardness of the shaped bodies obtained in accordance with the invention is particularly surprising, since semiorganic MOFs, after the shaping step, cannot be calcined at the high temperatures typically required for zeolites (generally 500 to 600°C, e.g. EP 1 468 731). The high temperatures are required to form a ceramic from the binder used, this bringing about the hardness of the zeolite shaped body (typical crush strength around 40-50 N, e.g. EP 1 467 811).

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MOFs decompose at these high temperatures due to the proportion of organic units present. Surprisingly, even much lower temperatures (e.g. 200°C) are sufficient to obtain shaped bodies of appropriate hardness.

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Experts in the field avoid using binders to avoid pore blocking as is outlined in WO2012/156436. Additionally surprisingly, the conventional binders used according to this invention do not cause excessive conglutination or blockage of the highly porous MOF structures having up to 20 times the surface area of zeolites. The resulting spherical MOF shaped bodies have high surface are-

as and consequently exhibit high methane adsorptions. Particularly surprisingly, it is possible to add relatively high amounts of binder (e.g. 20% by weight) without any dramatic reduction in surface area. Normally, the adsorption capacity of the related zeolites is reduced by adding the above-described conventional binders (EP 1 467 811). In the case of MOF materials, the use of commercial cement as a binder actually leads to MOF spheres having application properties similar to those of the MOF powder. The inventive adsorption system thus, completely surprisingly, has a wide range of standard (as in the case of zeolites) and unusual (e.g. cements) binder materials, and, for very different amounts of binder, very good application properties which can be adjusted precisely to the respective application via the type of binder used.

The inventive shaped bodies can be obtained by the process described with all kinds of MOF powders as described in the prior art and producible by the expert in the field. The inventive shaped bodies can have a somewhat oval to ideally spherical shape, in the form of smooth spheres or beads or with rough uneven surfaces. The spheroidal shaped bodies obtained in accordance with the invention also have a relatively wide particle size distribution. By sieving, it is possible to separate the spheres into fractions with narrow particle size distribution, as is also common practice in the industrial production of established adsorbents (zeolites, molecular sieves).

One aspect of the present invention is a method for preparing a shaped body in the form of spheres comprising the step of mixing a composition comprising the MOF and at least one liquid.

As liquids, it is possible to use, inter alia, preferably water or at least one alcohol such as, for example: a monoalcohol having from 1 to 4 carbon atoms, for example methanol, ethanol, n-propanol, isopropanol, 1-butanol, 2-butanol, 2-methyl-1-propanol or 2-methyl-2-propanol, or a mixture of water and at least one of the alcohols mentioned or a polyhydric alcohol such as a glycol, preferably a water-miscible polyhydric alcohol, either alone or as a mixture with water and/or at least one of the monohydric alcohols mentioned.

The at least one liquid preferred comprises water and/or aqueous solutions. In a very preferred embodiment the at least one liquid is water. In another very preferred embodiment the at least one liquid is a mixture of water and C₁ to C₄ organic alcohols.

The ratio of MOF to the amount of liquid(s) (based on weight) is in the range of from 1:0.1 to 1:10, preferred from 1:0.5 to 1:5, more preferred from 1:1 to 1:4, even more preferred from 1:1.5 to 1:3.

It is important that the components are added in a certain order. First, at least part of the MOF is charged into the mixer and part of the at least one liquid is added. Later the remaining amounts of the MOF and the liquid are added sequentially to keep a certain humidity level in the mixture

and let the granules consistently grow to spheres. In a preferred embodiment of the present invention the remaining amounts of the MOF and the liquid are dosed simultaneously.

5 The dosing rate is as such that the at least one liquid is always added in the form of a spray or droplets. Preferred the dosing rate is in the range of from 0.1 liter per hour (l h^{-1}) to 100 l h^{-1} , preferred from 0.5 l h^{-1} to 80 l h^{-1} , more preferred from 1 l h^{-1} to 30 l h^{-1} , even more preferred from 1 l h^{-1} to 10 l h^{-1} .

10 The term 'mixing' within the frame of this application is defined as follows: filling the components into a mixer and agitating the mixer.

Mixers comprise intensive mixers, rotary plates, marumerizers and any other equipment known to the expert. Preferred mixers are selected from the group consisting of intensive mixers, rotary plates, ballformers and marumerizers.

15 In a preferred embodiment the composition further comprises at least one additive, i.e. the concerning method comprises the step of mixing a composition comprising the MOF, the at least one liquid and at least one additive.

20 In a preferred embodiment the at least one additive comprises a binder, with the binder used basically being able to be any chemical compound which holds or draws other materials together to form a cohesive whole.

25 More preferred the at least one additive is a binder.

In a more preferred embodiment the at least one additive comprises a binder selected from the group consisting of inorganic oxides (preferred aluminum oxide), clays (preferred bentonite) and concrete.

30 Preferred binders are, for example, inter alia aluminum oxide or binders comprising aluminum oxide, as are described, for example, in WO 94/29408, silicon dioxide as described, for example, in EP 0 592 050 A1, mixtures of silicon dioxide and aluminum oxide as are described, for example, in WO 94/13584, clay minerals as are described, for example, in JP 03-037156 A, for example montmorillonite, kaolin, bentonite, halloysite, dickite, nacrite and anauxite, alkoxysilanes as are described, for example, in EP 0 102 544 B1, for example tetraalkoxysilanes such as tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, or for example trialkoxysilanes such as trimethoxysilane, triethoxysilane, tripropoxysilane, tributoxysilane, alkoxytitanates, for example tetraalkoxytitanates such as tetramethoxytitanate, tetraethoxytitanate, tetrapropoxytitanate, tetrabutoxytitanate, or for example trialkoxytitanates such as trimethoxytitanate, triethoxytitanate, tripropoxytitanate, tributoxytitanate, alkoxyzirconates, for example tetraalkoxyzirconates such as tetramethoxyzirconate, tetraethoxyzirconate, tetrapropoxyzirconate, tetrabutoxyzirconate, or for example

trialkoxyzirconates such as trimethoxyzirconate, triethoxyzirconate, tripropoxyzirconate, tributoxizirconate, silica soles, cements and/or amphiphilic substances

5 Further additives which can be used during the mixing process and added at any time during the process are, inter alia, amines or amine derivatives such as tetraalkylammonium compounds or amino alcohols and carbonate-comprising compounds such as calcium carbonate. Such further additives are described, for instance, in EP 0 389 041 A1, EP 0 200 260 A1 or WO 95/19222.

10 The order of the additives such as amines, binder, pasting agent, viscosity-increasing substance during mixing is in principle not critical.

Preferred additives comprise binders and/or pore forming agents. In a preferred embodiment the at least one additive comprises at least one binder.

15 Preferred binders are selected from the group consisting of inorganic oxides (preferred aluminum oxide), clays (preferred bentonite) and concrete.

20 The amount of the at least one binder based on the total weight of the shaped body is from 1 to 80 wt.-%, preferred 2 to 50 wt.-%, more preferred 3 to 30 wt.-%, even more preferred 4 to 20 wt.-%, even more preferred 5 to 10 wt.-%.

In a further embodiment the at least one additive comprises a pore forming agent. The pore forming agent is preferred selected from the group consisting of organic polymers, preferred methylcellulose, polyethylene oxide or mixtures thereof.

25 The mixing can be carried out at elevated temperatures, for example in the range from room temperature to 300°C, and/or under superatmospheric pressure, for example in the range from atmospheric pressure to a few hundred bar, and/or in a protective gas atmosphere, for example in the presence of at least one noble gas, nitrogen or a mixture of two or more thereof.

30 A method according to the invention is performed at a temperature of 100°C or less, preferred 80°C or less, more preferred at a temperature of 50°C or less, most preferred at a temperature of from 20°C to 50°C.

35 In a further, preferred embodiment, the shaped body obtained by mixing is subjected to at least one drying step which is generally carried out at a temperature in the range from 25 to 500°C, preferably in the range from 50 to 500°C and particularly preferably in the range from 100 to 350°C. It is likewise possible to carry out drying under reduced pressure or under a protective gas atmosphere.

40 The shaped bodies are preferred heated after the mixing or the drying step in a so-called activation step. The activation step is performed at a temperature of 300°C or less, preferred 250°C or less, more preferred at a temperature of 200°C or less.

Metal-organic frameworks (MOFs) are widely known. Preferred MOFs within the frame of this invention are those wherein the metal of the MOF is selected from the group consisting of Mg, Zn, Al or mixtures thereof, preferred Al.

In a preferred embodiment the MOF comprises

- aluminum; and
- fumarate, trimesate, 2-aminoterephthalic acid or 4,4',4''-benzene-1,3,5-triyl-tribenzoate or mixtures thereof.

The size of the shaped bodies that are yielded by the method are such that the smallest to largest diameters of the shaped bodies both are of from 1 to 50 mm, preferred 1.5 to 30 mm, more preferred 2 to 20 mm, even more preferred 2 to 15 mm. The minimum and maximum diameters are determined using a sliding calliper.

By sieving, the spheres can be separated into fractions with narrow particle size distribution.

A further objective of the invention is a shaped body in the form of spheres obtainable by a method as described before.

Another objective of the invention is a shaped body in the form of spheres obtained by a method as described before.

The shaped bodies are suitable for storage of a gas.

A preferred gas is a methane-containing mixture or methane. Another preferred gas is hydrogen. A further preferred gas is carbon dioxide (CO₂).

A further aspect of the present invention is accordingly a method for adsorbing, storing and/or releasing at least one gas by use of the metal-organic framework of the invention.

A further objective is the use of the shaped body for the uptake of at least one substance for the purposes of its storage, separation, controlled release, chemical reaction or as support. This concerns the use of the shaped body obtainable by a method as described before or obtained by a method as described before for the uptake of at least one substance for the purposes of its storage, separation, controlled release, chemical reaction or as support.

Preferred the at least one substance is a gas or gas mixture, preferred natural gas, shale gas or hydrogen.

Particularly preferred the at least one substance is natural gas or shale gas which is stored in vehicle tanks or gas containers or gas transporters such as ships and trucks.

Likewise, a further aspect of the present invention is accordingly a method of storing a gas, which comprises the step of bringing the gas into contact with a shaped body according to the invention.

5 Methane or methane-containing gases are particularly suitable for this storage.

Hydrogen is particularly suitable for this storage.

Carbon dioxide is also particularly suitable for this storage.

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In addition, the shaped body of the invention is suitable for separating a gas from a gas mixture.

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A further aspect of the present invention is accordingly the use of a shaped body according to the invention for separating a gas from a gas mixture.

Likewise, a further aspect of the present invention is accordingly a method of separating a gas from a gas mixture, which comprises the step: bringing a shaped body according to the invention into contact with the gas mixture.

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The gas mixture is, in particular, a gas mixture comprising methane and other gases. Here, methane is preferably removed from the gas mixture.

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Furthermore, the gas mixture can be a mixture comprising methane and water. Preference is given to removing gaseous water from the gas mixture. The gas mixture can be, for example, water-comprising natural gas. Other gases or volatile components which are preferably separated off are sulfur-based impurities in natural gas or shale gas like hydrogen sulfide or carbonyl sulfide.

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Likewise, the gas mixture can be a gas mixture comprising hydrogen.

Likewise, the gas mixture can be a gas mixture comprising carbon dioxide.

The present invention is illustrated by means of the examples below.

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Examples

The examples which follow describe the inventive spheronizing of MOF material. The MOF material used was produced according to WO 12/042410.

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The spheroidal shaped bodies obtained had a relatively wide particle size distribution. For each example, the minimum and maximum diameters are reported as determined using a sliding cal-

liper. By sieving, the spheres can be separated into fractions with narrow particle size distribution.

5 Bulk densities of sphere packings were determined using a jolting volumeter type STAV II from J. Engelsmann AG. The machine has been tested according to DIN ISO 787 by the manufacturer. A weighed amount of the respective sample was put into a 1000 or 100 mL scaled cylinder. After tapping the cylinder 3000 times, the resulting volume of the packing was determined and the density calculated by dividing sample weight by sample volume.

10 The density of spheres was determined by weighing a selected sphere, measuring its diameter with a sliding calliper and then dividing weight by volume (the latter being calculated via the diameter).

15 The specific surface area of the spheres was calculated by applying the Langmuir model according to DIN 66131 and 66134.

The crush strength is defined within the meaning of the present invention as lateral pressure resistance to pressure and can be measured with a hardness grading device by Zwick.

20 Example 1: Spheronizing with 20% by weight of K10 clay
Aluminum fumarate MOF (1000 g) was initially charged in an Eirich intensive mixer (model: R02, RV02). K10 clay (250 g) was added and mixed with the MOF. A manual pressure sprayer was used to spray on demineralized water (2200 g) with continuous movement of the mixture over 50 minutes. Within this time, a second portion of aluminum fumarate MOF (160 g) was
25 added. After completing the addition of water, the spherical shaped bodies formed were dried (12 h, 100°C) and activated (5 h, 200°C). 1058 g of spheres were obtained.

Diameter:	2-15 mm
Bulk density of sphere packing:	0.54 g/ml
Average density of spheres:	0.57-1.10 g/ml
30 Crush strength:	80 N
Langmuir surface area:	952 m ² /g (surface area of the binder: 377 m ² /g)
Pore volume:	0.43 cm ³ /g (by means of mercury porosimetry)
Methane absorption:	52 g/l (at 298 K, 50 bar)

35 Example 2: Spheronizing with 20% by weight of bentonite
Aluminum fumarate MOF (1000 g) was initially charged in an Eirich intensive mixer (model: R02, RV02). Bentonite (250 g) was added and mixed with the MOF. A manual pressure sprayer was used to spray on demineralized water (2069 g) with continuous movement of the mixture over 30 minutes. Within this time, a second portion of aluminum fumarate MOF (70 g) was add-
40 ed. After completing the addition of water, the spherical shaped bodies formed were dried (12 h, 100°C) and activated (5 h, 200°C). 1038 g of spheres were obtained.

Diameter:	4-15 mm
Bulk density of sphere packing:	0.48 g/ml
Average density of spheres:	0.47-1.09 g/ml
Crush strength:	64 N
5 Langmuir surface area:	966 m ² /g (surface area of the binder: 508 m ² /g)
Pore volume:	0.54 cm ³ /g (by means of mercury porosimetry)
Methane absorption:	50 g/l (at 298 K, 50 bar)

Example 3: Spheronizing with 20% by weight of Pural SB

- 10 Aluminum fumarate MOF (1000 g) was initially charged in an Eirich intensive mixer (model: R02, RV02). Pural SB (250 g) was added and mixed with the MOF. A manual pressure sprayer was used to spray on a mixture of formic acid (7.5 g) and demineralized water (100 g) with continuous movement of the mixture. Thereafter, pure demineralized water (1795 g) was sprayed on with continuous movement of the mixture over 35 minutes. After completing the addition of
- 15 water, the spherical shaped bodies formed were dried (12 h, 100°C) and activated (5 h, 200°C). 900 g of spheres were obtained.

Diameter:	2-8 mm
Bulk density of sphere packing:	0.39 g/ml
Average density of spheres:	0.27-1.15 g/ml
20 Crush strength:	24 N
Langmuir surface area:	812 m ² /g (surface area of the binder: 381 m ² /g)
Pore volume:	0.54 cm ³ /g (by means of mercury porosimetry)
Methane absorption:	50 g/l (at 298 K, 50 bar)

25 Example 4: Spheronizing with 3% by weight of Secar 80 cement

- Aluminum fumarate MOF (1000 g) was initially charged in an Eirich intensive mixer (model: R02, RV02). Secar 80 cement (30 g) was added and mixed with the MOF. A manual pressure sprayer was used to spray on demineralized water (1895 g) with continuous movement of the mixture over 50 minutes. After completing the addition of water, the spherical shaped bodies
- 30 formed were dried (12 h, 100°C) and activated (5 h, 200°C). 910 g of spheres were obtained.

Diameter:	4-9 mm
Bulk density of sphere packing:	0.38 g/ml
Average density of spheres:	0.49-0.87 g/ml
Crush strength:	35 N
35 Langmuir surface area:	1078 m ² /g (surface area of the binder: 107 m ² /g)
Pore volume:	0.66 cm ³ /g (by means of mercury porosimetry)
Methane absorption:	51 g/l (at 298 K, 50 bar)

Example 5: Spheronizing without additive

- 40 Aluminum fumarate MOF (1000 g) was initially charged in an Eirich intensive mixer (model: R02, RV02). A manual pressure sprayer was used to spray on demineralized water (1900 g) with continuous movement of the mixture over 50 minutes. After completing the addition of wa-

ter, the spherical shaped bodies formed were dried (12 h, 100°C) and activated (5 h, 200°C). 735 g of spheres were obtained.

Diameter: 3-8 mm

Bulk density of sphere packing: 0.39 g/ml

5 Average density of spheres: 0.46-1.21 g/ml

Crushing strength: 34 N

Langmuir surface area: 1138 m²/g

Pore volume: 0.68 cm³/g (by means of mercury porosimetry)

Methane absorption: 52 g/l (at 298 K, 50 bar)

Claims

1. A method for preparing a shaped body in the form of spheres comprising the step of mixing a composition comprising the MOF and at least one liquid, preferred water.
2. A method of claim 1 comprising the step of mixing a composition comprising the MOF, the at least one liquid and at least one additive.
3. A method of claim 1 or 2, wherein the at least one additive comprises a binder selected from the group consisting of inorganic oxides (preferred aluminum oxide), clays (preferred bentonite) and concrete.
4. A method of claim 3, wherein the amount of the at least one binder additive based on the total weight of the shaped body is from 1 to 80 wt.-%, preferred 2 to 50 wt.-%, more preferred 3 to 30 wt.-%, even more preferred 4 to 20 wt.-%, even more preferred 5 to 10 wt.-%.
5. A method of any of claims 1 to 4, wherein the at least one additive comprises a pore forming agent selected from the group consisting of organic polymers, preferred methylcellulose, polyethylene oxide or mixtures thereof.
6. A method of any one of claims 1 to 5 at a temperature of 100°C or less, preferred 80°C or less, more preferred at a temperature of 50°C or less, most preferred at a temperature of from 20°C to 50°C.
7. A method of any one of claims 1 to 6 with an activation step at a temperature of 300°C or less, preferred 250°C or less, more preferred at a temperature of 200°C or less.
8. A method of any one of claims 1 to 7, wherein the metal of the MOF is selected from the group consisting of Mg, Zn, Al or mixtures thereof, preferred Al.
9. A method of any one of claims 1 to 8, wherein the MOF comprises
 - aluminum; and
 - fumarate, trimesate, 2-aminoterephthalic acid or 4,4',4''-benzene-1,3,5-triyl-tribenzoate or mixtures thereof.
10. A method of any one of claims 1 to 9, wherein the smallest to largest diameters of the shaped bodies are of from 1 to 50 mm, preferred 1.5 to 30 mm, more preferred 2 to 20 mm, even more preferred 2 to 15 mm.
11. A shaped body in the form of spheres obtainable by a method according to any of claims 1 to 10.

12. A shaped body in the form of spheres obtained by a method according to any of claims 1 to 10.
- 5 13. Use of a shaped body of claim 11 or claim 12 for the uptake of at least one substance for the purposes of its storage, separation, controlled release, chemical reaction or as support.
- 10 14. Use of a shaped body prepared by a method of any one of claims 1 to 10 for the uptake of at least one substance for the purposes of its storage, separation, controlled release, chemical reaction or as support.
- 15 15. The use of claim 13 or 14, wherein the at least one substance is a gas or gas mixture, preferred natural gas, shale gas or hydrogen.
16. The use of any one of claims 13 to 15, wherein the at least one substance is natural gas or shale gas which is stored in vehicle tanks or gas containers or gas transporters such as ships and trucks.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/051226

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J2/06 B01J2/14 B01J20/22 B01J20/28 B01J20/30
ADD.

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)

B01D B01J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/051904 A1 (PRAXAIR TECHNOLOGY INC [US]; BARRETT PHILIP A [US]; STEPHENSON NEIL AN) 2 May 2008 (2008-05-02) claims 2-5 page 25, line 28 page 7, line 16 - page 8, line 16 page 25, line 6 - line 10 page 25, line 16 - line 30 -----	1-16
X	US 2011/011805 A1 (SCHUBERT MARKUS [DE] ET AL) 20 January 2011 (2011-01-20) claims 9-16 paragraph [0056] - paragraphs [0059], [0062] paragraphs [0068], [0070], [0071], [0075] - [0079] ----- -/--	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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International application No

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