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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
26 March 2015 (26.03.2015)

WIPO | PCT

(10) **International Publication Number**
WO 2015/040593 A1

WO 2015/040593 A1

(51) **International Patent Classification**:
B01J 20/34 (2006.01) ***B01J 20/22*** (2006.01)
B01D 11/02 (2006.01) ***B01J 20/282*** (2006.01)

(21) **International Application Number**:
PCT/IB2014/064724

(22) **International Filing Date**:
22 September 2014 (22.09.2014)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
13185532.2 23 September 2013 (23.09.2013) EP

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:
- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title**: PROCESS FOR THE RECOVERY OF COMPONENTS FORMING A METAL-ORGANIC FRAMEWORK MATERIAL

(57) **Abstract**: The present invention relates to a process for the recovery of an at least bidentate organic compound comprised in a porous metal-organic framework material, the material comprising the at least bidentate organic compound coordinated to at least one metal ion, the process comprising the steps of (a) treating the metal-organic framework material with an acidic or alkaline liquid; (b) optionally separating off solid residue; and (c) isolating the at least bidentate organic compound.

Process for the recovery of components forming a metal-organic framework material

Description

The present invention relates a process for the recovery of an at least bidentate organic compound comprised in a porous metal-organic framework material, the material comprising the at least bidentate organic compound coordinated to at least one metal ion.

The usage of metal-organic framework material as adsorbents for example in natural gas storage tanks for automotive requires a careful look into the whole lifecycle of the application. With respect to automotive applications after exceeding the lifetime of the vehicle the tanks containing the metal-organic framework material will be dismantled and the adsorbent has to either be disposed or treated somehow else. Most beneficial from both ecological and economical view would be a simple recycling procedure allowing to re-obtain at least the organic linker in high yields and the reuse in the corresponding synthesis of fresh metal-organic framework material.

Thus, an object of the present invention is to find a simple solution for recycling of components (or at least the organic ligand) forming a metal-organic framework material on a solid ecological and economical foundation.

The object is achieved by a process for the recovery of an at least bidentate organic compound comprised in a porous metal-organic framework material, the material comprising the at least bidentate organic compound coordinated to at least one metal ion, the process comprising the steps of

(a) treating the metal-organic framework material with an acidic or alkaline liquid;
(b) optionally separating off solid residue;
(c) isolating the at least bidentate organic compound.

It was surprisingly found that the at least bidentate organic compound (ligand) can be recovered in high yields and good purities so that the recovered ligand can be re-used for example for the preparation of new metal-organic framework materials. Furthermore also the metal ion can be recovered and re-used.

According to the present invention an at least bidentate organic compound (also called “linker”), which participates in the formation of a metal-organic framework material (also called “metal-organic framework” or “MOF”) by coordinating at least one metal ion is recovered.

The porous metal-organic framework can be present in powder form or as shaped bodies.

Such metal-organic frameworks (MOFs) are known in the prior art and are described, for example, in US 5,648,508, EP-A-0 790 253, M. O'Keeffe et al., J. Sol. State Chem., 152 (2000), pages 3 to 20, H. Li et al., Nature 402, (1999), page 276, M. Eddaoudi et al., Topics in Catalysis 9, (1999), pages 105 to 111, B. Chen et al., Science 291, (2001), pages 1021 to 1023, DE-A-

101 11 230, DE-A 10 2005 053430, WO-A 2007/054581, WO-A 2005/049892 and WO-A 2007/023134.

The general suitability of metal-organic frameworks for the sorption of gases and liquids is described, for example, in WO-A 2005/003622 and EP-A 1 702 925.

The metal-organic frameworks of the present invention comprise pores, in particular micropores and/or mesopores. Micropores are defined as pores having a diameter of 2 nm or less and mesopores are defined by a diameter in the range from 2 to 50 nm, in each case in accordance with the definition given in Pure & Applied Chem. 57 (1983), 603 - 619, in particular on page 606. The presence of micropores and/or mesopores can be checked by means of sorption measurements which determine the uptake capacity of the MOF for nitrogen at 77 Kelvin in accordance with DIN 66131 and/or DIN 66134.

The specific surface area, calculated according to the Langmuir model (DIN 66131, 66134), of a MOF in powder form is preferably greater than 1 m^2/g, more preferably greater than 10 m^2/g, more preferably greater than 100 m^2/g, more preferably above 300 m^2/g, more preferably greater than 700 m^2/g, even more preferably greater than 800 m^2/g.

Shaped bodies comprising metal-organic frameworks can have a lower active surface area, but this is preferably greater than 1 m^2/g, more preferably greater than 10 m^2/g, even more preferably greater than 100 m^2/g.

However, the metal-organic framework material in the process of the present invention is already used in any application so that the pores can be already occupied by sorbed material, like gases, liquids or the like. Thus, according to the present invention the term “porous” means a porous material, where the porosity is or was given. Thus the porosity can be measured directly or after removal of such sorbed material (or at least partly removed), e.g. by heat treatment.

As a consequence the metal-organic framework material can be unused or used material, preferably used material is employed.

The metal component in the framework according to the present invention is preferably selected from groups Ia, IIa, IIIa, IVa to VIIIa and Ib to VIb. Particular preference is given to Li, Na, Mg, Ca, Sr, Ba, Sc, Y, Ln, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ro, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb and Bi, where Ln represents lanthanides.

Lanthanides are La, Ce, Pr, Nd, Pm, Sm, En, Gd, Tb, Dy, Ho, Er, Tm, Yb.

With regard to the ions of these elements, particular mention may be made of Li^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Y^{3+}, Ln^{3+}, Ti^{4+}, Zr^{4+}, Hf^{4+}, V^{4+}, V^{3+}, V^{2+}, Nb^{3+}, Ta^{3+}, Cr^{3+}, Mo^{3+}, W^{3+}, Mn^{3+}, Mn^{2+}, Re^{3+}, Re^{2+}, Fe^{3+}, Fe^{2+}, Ru^{3+}, Ru^{2+}, Os^{3+}, Os^{2+}, Co^{3+}, Co^{2+}, Rh^{2+}, Rh^+, Ir^{2+}, Ir^+, Ni^{2+}, Ni^+,

Pd^{2+}, Pd^{+}, Pt^{2+}, Pt^{+}, Cu^{2+}, Cu^{+}, Ag^{+}, Au^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Si^{4+}, Si^{2+}, Ge^{4+}, Ge^{2+}, Sn^{4+}, Sn^{2+}, Pb^{4+}, Pb^{2+}, As^{5+}, As^{3+}, As^{+}, Sb^{5+}, Sb^{3+}, Sb^{+}, Bi^{5+}, Bi^{3+} and Bi^{+}.

Particular preference is given to Mg, Al, Li, Ca, Zr, Ti, V, Cr, Mo, Fe, Co, Cu, Ni, Zn, La. Greater preference is given to Al, Mo, Mg, Fe, Cu and Zn. Very particular preference is given to Al, Cu, Mg and Zn, especially Al, Cu and Zn.

The term "at least bidentate organic compound" refers to an organic compound which comprises at least one functional group which is able to form at least two coordinate bonds to a given metal ion and/or a coordinate bond to each of two or more, preferably two, metal atoms.

As functional groups via which the coordinate bonds mentioned can be formed, particular mention may be made of, for example, the following functional groups: $-CO_2H$, $-CS_2H$, $-NO_2$, $-B(OH)_2$, $-SO_3H$, $-Si(OH)_3$, $-Ge(OH)_3$, $-Sn(OH)_3$, $-Si(SH)_4$, $-Ge(SH)_4$, $-Sn(SH)_3$, $-PO_3H$, $-AsO_3H$, $-AsO_4H$, $-P(SH)_3$, $-As(SH)_3$, $-CH(RSH)_2$, $-C(RSH)_3$, $-CH(RNH_2)_2$, $-C(RNH_2)_3$, $-CH(ROH)_2$, $-C(ROH)_3$, $-CH(RCN)_2$, $-C(RCN)_3$, where R is, for example, preferably an alkylene group having 1, 2, 3, 4 or 5 carbon atoms, for example a methylene, ethylene, n-propylene, i-propylene, n-butylene, i-butylene, tert-butylene or n-pentylene group, or an aryl group comprising 1 or 2 aromatic rings, for example 2 C_6 rings, which may, if appropriate, be fused and may be independently substituted by at least one substituent in each case and/or may comprise, independently of one another, at least one heteroatom such as N, O and/or S. In likewise preferred embodiments, functional groups in which the abovementioned radical R is not present are possible. Such groups are, inter alia, $-CH(SH)_2$, $-C(SH)_3$, $-CH(NH_2)_2$, $-C(NH_2)_3$, $-CH(OH)_2$, $-C(OH)_3$, $-CH(CN)_2$ or $-C(CN)_3$.

The at least two functional groups can in principle be any suitable organic compound, as long as it is ensured that the organic compound in which these functional groups are present is capable of forming the coordinate bond and producing the framework.

The organic compounds which comprise the at least two functional groups are preferably derived from a saturated or unsaturated aliphatic compound or an aromatic compound or a both aliphatic and aromatic compound.

The term “derived from” means that the organic compound is present in the metal-organic framework material in fully or partly deprotonated form or without any deprotonation. For example a carboxylic acid used as at least bidentate organic compound can be present in the metal-organic framework at least partly as carboxylate. However, also the carboxylic acid may be present. The term “derived from” also encompasses substituted derivatives of the organic compounds; however, this is not preferred. Suitable substituents are hydroxyl, methyl, ethyl, fluoro, chloro, bromo, amino (NH_2), phenyl, benzyl.

The aliphatic compound or the aliphatic part of the both aliphatic and aromatic compound can be linear and/or branched and/or cyclic, with a plurality of rings per compound also being possible. More preferably, the aliphatic compound or the aliphatic part of the both aliphatic and aromatic compound comprises from 1 to 15, more preferably from 1 to 14, more preferably from 1 to 13, more preferably from 1 to 12, more preferably from 1 to 11 and particularly preferably from 1 to 10, carbon atoms, for example 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 carbon atoms. Particular preference is here given to, inter alia, methane, adamantane, acetylene, ethylene or butadiene.

The aromatic compound or the aromatic part of the both aromatic and aliphatic compound can have one or more rings, for example two, three, four or five rings, with the rings being able to be separate from one another and/or at least two rings being able to be present in fused form. The aromatic compound or the aromatic part of the both aliphatic and aromatic compound particularly preferably has one, two or three rings, with one or two rings being particularly preferred. Furthermore, each ring of the specified compound can independently comprise at least one heteroatom such as N, O, S, B, P, Si, Al, preferably N, O and/or S. The aromatic compound or the aromatic part of the both aromatic and aliphatic compound more preferably comprises one or two C_6 rings which are present either separately or in fused form. Particular mention may be made of benzene, naphthalene and/or biphenyl and/or bipyridyl and/or pyridyl as aromatic compounds.

The at least bidentate organic compound is more preferably an aliphatic or aromatic, acyclic or cyclic hydrocarbon which has from 1 to 18, preferably from 1 to 10 and in particular 6, carbon atoms and also has exclusively 2, 3 or 4 carboxyl groups as functional groups.

Preferably, the at least bidentate organic compound is derived from a di- tri- or tetracarbocyclic acid.

For example, the at least bidentate organic compound is derived from a dicarboxylic acid such as oxalic acid, succinic acid, tartaric acid, 1,4-butanedicarboxylic acid, 1,4-butenedicarboxylic acid, 4-oxopyran-2,6-dicarboxylic acid, 1,6-hexanedicarboxylic acid, decanedicarboxylic acid, 1,8-heptadecanedicarboxylic acid, 1,9-heptadecanedicarboxylic acid, heptadecanedicarboxylic acid, acetylenedicarboxylic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 2,3-pyridinedicarboxylic acid, pyridine-2,3-dicarboxylic acid, 1,3-butadiene-1,4-dicarboxylic acid, 1,4-benzenedicarboxylic acid, p-benzenedicarboxylic acid, imidazole-2,4-dicarboxylic acid, 2-methylquinoline-3,4-dicarboxylic acid, quinoline-2,4-dicarboxylic acid, quinoxaline-2,3-dicarboxylic acid, 6-chloroquinoxaline-2,3-dicarboxylic acid, 4,4'-diaminophenylmethane-3,3'-dicarboxylic acid, quinoline-3,4-dicarboxylic acid, 7-chloro-4-hydroxyquinoline-2,8-dicarboxylic acid, diimidecarboxylic acid, pyridine-2,6-dicarboxylic acid, 2-methylimidazole-4,5-dicarboxylic acid, thiophene-3,4-dicarboxylic acid, 2-isopropylimidazole-4,5-dicarboxylic acid, tetrahydropyrane-4,4-dicarboxylic acid, perylene-3,9-dicarboxylic acid, perylenedicarboxylic acid, Pluriol E 200-dicarboxylic acid, 3,6-dioxaoctanedicarboxylic acid, 3,5-cyclohexadiene-1,2-dicarboxylic acid, octadicarboxylic acid, pentane-3,3-carboxylic acid, 4,4'-diamino-1,1'-diphenyl-3,3'-dicarboxylic acid, 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid, benzidine-3,3'-dicarboxylic acid, 1,4-bis(phenylamino)benzene-2,5-dicarboxylic acid, 1,1'-binaphthyldicarboxylic acid, 7-chloro-8-methylquinoline-2,3-dicarboxylic acid, 1-anilinoanthraquinone-2,4'-dicarboxylic acid, polytetrahydrofuran 250-dicarboxylic acid, 1,4-bis(carboxymethyl)piperazine-2,3-dicarboxylic acid, 7-chloroquinoline-3,8-dicarboxylic acid, 1-(4-carboxy)phenyl-3-(4-chloro)phenylpyrazoline-4,5-dicarboxylic acid, 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid, phenylindandicarboxylic acid, 1,3-dibenzyl-2-oxoimidazolidine-4,5-dicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, naphthalene-1,8-dicarboxylic acid, 2-benzoylbenzene-1,3-dicarboxylic acid, 1,3-dibenzyl-2-oxoimidazolidine-4,5-cis-dicarboxylic acid, 2,2'-biquinoline-4,4'-dicarboxylic acid, pyridine-3,4-dicarboxylic acid, 3,6,9-trioxaundecanedicarboxylic acid, hydroxybenzophenon-dicarboxylic acid, Pluriol E 300-dicarboxylic acid, Pluriol E 400-dicarboxylic acid, Pluriol E 600-dicarboxylic acid, pyrazole-3,4-dicarboxylic acid, 2,3-pyrazinedicarboxylic acid, 5,6-dimethyl-2,3-pyrazinedicarboxylic acid, 4,4'-diamino(diphenyl ether)diimidedicarboxylic acid, 4,4'-diaminodiphenylmethanediimidedicarboxylic acid, 4,4'-diamino(diphenyl sulfone)diimid edicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 1,3-adamantanedicarboxylic acid, 1,8-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid, 8-methoxy-2,3-naphthalenedicarboxylic acid, 8-nitro-2,3-naphthalenecarboxylic acid, 8-sulfo-2,3-naphthalenedicarboxylic acid, anthracene-2,3-dicarboxylic acid, 2',3'-diphenyl-p-terphenyl-4,4''-dicarboxylic acid, (diphenyl ether)-4,4'-dicarboxylic acid, imidazole-4,5-dicarboxylic acid, 4(1H)-oxothiochromene-2,8-dicarboxylic acid, 5-tert-butyl-1,3-benzenedicarboxylic acid, 7,8-quinolinedicarboxylic acid, 4,5-imidazoledicarboxylic acid, 4-cyclohexene-1,2-dicarboxylic acid, hexatriacontanedicarboxylic acid, tetradecanedicarboxylic acid, 1,7-heptadicarboxylic acid, 5-hydroxy-1,3-benzenedicarboxylic acid, 2,5-dihydroxy-1,4-dicarboxylic acid, pyrazine-2,3-dicarboxylic acid, furan-2,5-dicarboxylic acid, 1-nonene-6,9-dicarboxylic acid, eicosenedicarboxylic acid, 4,4'-dihydroxydiphenylmethane-3,3'-dicarboxylic acid, 1-amino-4-methyl-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid, 2,5-pyridinedicarboxylic acid, cyclohexene-2,3-dicarboxylic acid, 2,9-dichlorofluorubin-4,11-dicarboxylic acid, 7-chloro-3-methylquinoline-6,8-dicarboxylic acid, 2,4-dichlorobenzophenon-2',5'-dicarboxylic acid, 1,3-benzenedicarboxylic acid, 2,6-pyridinedicarboxylic acid, 1-methylpyrrole-3,4-dicarboxylic acid, 1-benzyl-1H-pyrrole-3,4-dicarboxylic acid, anthraquinone-1,5-dicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2-nitrobenzene-1,4-dicarboxylic acid, heptane-1,7-dicarboxylic acid, cyclobutane-1,1-dicarboxylic acid, 1,14-tetradecanedicarboxylic acid, 5,6-dehydronorbornane-2,3-dicarboxylic acid, 5-ethyl-2,3-pyridinedicarboxylic acid or camphordicarboxylic acid.

Furthermore, the at least bidentate organic compound is more preferably one of the dicarboxylic acids mentioned by way of example above as such (with further substitution).

For example, the at least bidentate organic compound can be derived from a tricarboxylic acid such as

2-hydroxy-1,2,3-propanetricarboxylic acid, 7-chloro-2,3,8-quinolinetricarboxylic acid, 1,2,3-, 1,2,4-benzenetricarboxylic acid, 1,2,4-butanetricarboxylic acid, 2-phosphono-1,2,4-butanetricarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1-hydroxy-1,2,3-propanetricarboxylic acid, 4,5-dihydro-4,5-dioxo-1H-pyrrolo[2,3-F]quinoline-2,7,9-tricarboxylic acid, 5-acetyl-3-amino-6-methylbenzene-1,2,4-tricarboxylic acid, 3-amino-5-benzoyl-6-methylbenzene-1,2,4-tricarboxylic acid, 1,2,3-propanetricarboxylic acid or aurintricarboxylic acid.

Furthermore, the at least bidentate organic compound is more preferably one of the tricarboxylic acids mentioned by way of example above as such (without further substitution).

Examples of an at least bidentate organic compound derived from a tetracarboxylic acid are

1,1-dioxidoperylo[1,12-BCD]thiophene-3,4,9,10-tetracarboxylic acid, perylenetetracarboxylic acids such as perylene-3,4,9,10-tetracarboxylic acid or (perylene-1,12-sulfone)-3,4,9,10-tetracarboxylic acid, butanetetracarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid or meso-1,2,3,4-butanetetracarboxylic acid, decane-2,4,6,8-tetracarboxylic acid, 1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, 1,2,11,12-dodecanetetracarboxylic acid, 1,2,5,6-hexanetetracarboxylic acid, 1,2,7,8-octanetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid, 1,2,9,10-decanetetracarboxylic acid, benzophenontetracarboxylic acid, 3,3',4,4'-benzophenontetracarboxylic acid, tetrahydrofurantetracarboxylic acid or cyclopentanetetracarboxylic acids such as cyclopentane-1,2,3,4-tetracarboxylic acid.

Furthermore, the at least bidentate organic compound is more preferably one of the tetracarboxylic acids mentioned by way of example above as such (without further substitution).

Very particular preference is given to optionally at least monosubstituted aromatic dicarboxylic, tricarboxylic or tetracarboxylic acids having one, two, three, four or more rings, with each of the rings being able to comprise at least one heteroatom and two or more rings being able to comprise identical or different heteroatoms. For example, preference is given to one-ring dicarboxylic acids, one-ring tricarboxylic acids, one-ring tetracarboxylic acids, two-ring dicarboxylic acids, two-ring tricarboxylic acids, two-ring tetracarboxylic acids, three-ring dicarboxylic acids, three-ring tricarboxylic acids, three-ring tetracarboxylic acids, four-ring dicarboxylic acids, four-ring tricarboxylic acids and/or four-ring tetracarboxylic acids. Suitable heteroatoms are, for example, N, O, S, B, P, and preferred heteroatoms are N, S and/or O. Suitable substituents here are, inter alia, -OH, a nitro group, an amino group and an alkyl or alkoxy group.

Particularly preferred at least bidentate organic compounds are imidazolates such as 2-methylimidazolate, acetylenedicarboxylic acid (ADC), camphordicarboxylic acid, fumaric acid, succinic acid, benzenedicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid (BDC), aminoterephthalic acid, naphthalenedicarboxylic acids (NDC), biphenyldicarboxylic acids such as 4,4'-biphenyldicarboxylic acid (BPDC), pyrazinedicarboxylic acids such as 2,5-pyrazinedicarboxylic acid, bipyridinedicarboxylic acids such as 2,2'-bipyridinedicarboxylic acids such as 2,2'-bipyridine-5,5’-dicarboxylic acid, benzenetricarboxylic acids such as 1,2,3-, 1,2,4-benzenetricarboxylic acid or 1,3,5-benzenetricarboxylic acid (BTC), benzenetetracarboxylic acid, adamantanetetracarboxylic acid (ATC), adamantanedibenzoate (ADB), benzenetribenzoate (BTB), methanetetrabenzoate (MTB), adamantanetetrabenzoate or dihydroxyterephthalic acids such as 2,5-dihydroxyterephthalic acid (DHBDC), tetrahydropyrene-2,7-dicarboxylic acid (HPDC), biphenyltetracarboxylic acid (BPTC).

Very particular preference is given to using, inter alia, phthalic acid, isophthalic acid, terephthalic acid, 2,6-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 1,2,3-benzenetricarboxylic acid, 1,2,4-benzenetricarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, aminoBDC, fumaric acid, biphenyldicarboxylate, 1,5- and 2,6-naphthalenedicarboxylic acid, tert-butylisophthalic acid, dihydroxybenzoic acid, BTB, HPDC, BPTC.

Even more preferred are 1,3,5-tri-(4-carboxyphenyl)-benzene, dihydroxyterephthalic acid, benzene-tricarboxylic acid (especially 1,3,5-BTC) and fumaric acid, especially BTB, BTC and fumaric acid. Even more preferred BTB.

Apart from these at least bidentate organic compounds, the metal-organic framework can also comprise one or more monodentate ligands and/or one or more at least bidentate ligands which are not derived from a dicarboxylic, tricarboxylic or tetracarboxylic acid.

Apart from these at least bidentate organic compounds, the metal-organic framework can also comprise one or more monodentate ligands.

Suitable solvents for preparing the metal-organic framework are, inter alia, ethanol, dimethylformamide, toluene, methanol, chlorobenzene, diethylformamide, dimethyl sulfoxide, water, hydrogen peroxide, methylamine, sodium hydroxide solution, N-methylpyrrolidone ether, acetonitrile, benzyl chloride, triethylamine, ethylene glycol and mixtures thereof. Further metal ions, at least bidentate organic compounds and solvents for the preparation of MOFs are described, inter alia, in US-A 5,648,508 or DE-A 101 11 230.

The pore size of the metal-organic framework can be controlled by selection of the appropriate ligand and/or the at least bidentate organic compound. In general, the larger the organic compound, the larger the pore size. The pore size is preferably from 0.2 nm to 30 nm, particularly preferably in the range from 0.3 nm to 3 nm, based on the crystalline material.

However, larger pores whose size distribution can vary also occur in a shaped body comprising a metal-organic framework. Preference is nevertheless given to more than 50% of the total pore volume, in particular more than 75%, being made up by pores having a pore diameter of up 1000 nm. However, preference is given to a major part of the pore volume being made up by pores from two diameter ranges. It is therefore more preferred that more than 25% of the total pore volume, in particular more than 50% of the total pore volume, is formed by pores which are in a diameter range from 100 nm to 800 nm and that more than 15% of the total pore volume, in particular more than 25% of the total pore volume, is formed by pores which are in a diameter range up to 10 nm. The pore distribution can be determined by means of mercury porosimetry. However since used material typically has adsorbed agents in the pores a measurement of the pore size may be carried out after removing such agents, e.g. by thermal treatment.

Examples of metal-organic frameworks are given below. In addition to the designation of the framework, the metal and the at least bidentate ligand, the solvent and the cell parameters (angles α, β and γ and the dimensions A, B and C in Å) are indicated. The latter were determined by X-ray diffraction.

MOF-n	Constituents Molar ratio M+L	Solvents	α	β	γ	a	b	c	Space group
MOF-0	$Zn(NO_3)_2 \cdot 6H_2O$ $H_3(BTC)$	ethanol	90	90	120	16.711	16.711	14.189	P6(3)/Mcm
MOF-2	$Zn(NO_3)_2 \cdot 6H_2O$ (0.246 mmol) $H_2(BDC)$ 0.241 mmol)	DMF toluene	90	102.8	90	6.718	15.49	12.43	P2(1)/n
MOF-3	$Zn(NO_3)_2 \cdot 6H_2O$ (1.89 mmol) $H_2(BDC)$ (1.93mmol)	DMF MeOH	99.72	111.11	108.4	9.726	9.911	10.45	P-1
MOF-4	$Zn(NO_3)_2 \cdot 6H_2O$ (1.00 mmol) $H_3(BTC)$ (0.5 mmol)	ethanol	90	90	90	14.728	14.728	14.728	P2(1)3
MOF-5	$Zn(NO_3)_2 \cdot 6H_2O$ (2.22 mmol) $H_2(BDC)$ (2.17 mmol)	DMF chlorobenzene	90	90	90	25.669	25.669	25.669	Fm-3m
MOF-38	$Zn(NO_3)_2 \cdot 6H_2O$ (0.27 mmol) $H_3(BTC)$ (0.15 mmol)	DMF chlorobenzene	90	90	90	20.657	20.657	17.84	I4cm
MOF-31 $Zn(ADC)_2$	$Zn(NO_3)_2 \cdot 6H_2O$ 0.4 mmol $H_2(ADC)$ 0.8 mmol	ethanol	90	90	90	10.821	10.821	10.821	Pn(-3)m
MOF-12 $Zn_2(ATC)$	$Zn(NO_3)_2 \cdot 6H_2O$ 0.3 mmol $H_4(ATC)$ 0.15 mmol	ethanol	90	90	90	15.745	16.907	18.167	Pbca
MOF-20 ZnNDC	$Zn(NO_3)_2 \cdot 6H_2O$ 0.37 mmol H_2NDC 0.36 mmol	DMF chlorobenzene	90	92.13	90	8.13	16.444	12.807	P2(1)/c

MOF-n	Constituents Molar ratio M+L	Sol-vents	α	β	γ	a	b	c	Space group
MOF-37	$Zn(NO_3)_2 \cdot 6H_2O$ 0.2 mmol H_2NDC 0.2 mmol	DEF chloro-benzene	72.38	83.16	84.33	9.952	11.576	15.556	P-1
MOF-8 Tb_2 (ADC)	$Tb(NO_3)_3 \cdot 5H_2O$ 0.10 mmol H_2ADC 0.20 mmol	DMSO MeOH	90	115.7	90	19.83	9.822	19.183	C2/c
MOF-9 Tb_2 (ADC)	$Tb(NO_3)_3 \cdot 5H_2O$ 0.08 mmol H_2ADB 0.12 mmol	DMSO	90	102.09	90	27.056	16.795	28.139	C2/c
MOF-6	$Tb(NO_3)_3 \cdot 5H_2O$ 0.30 mmol H_2 (BDC) 0.30 mmol	DMF MeOH	90	91.28	90	17.599	19.996	10.545	P21/c
MOF-7	$Tb(NO_3)_3 \cdot 5H_2O$ 0.15 mmol H_2(BDC) 0.15 mmol	H_2O	102.3	91.12	101.5	6.142	10.069	10.096	P-1
MOF-69A	$Zn(NO_3)_2 \cdot 6H_2O$ 0.083 mmol 4,4'BPDC 0.041 mmol	DEF H_2O_2 $MeNH_2$	90	111.6	90	23.12	20.92	12	C2/c
MOF-69B	$Zn(NO_3)_2 \cdot 6H_2O$ 0.083 mmol 2,6-NCD 0.041 mmol	DEF H_2O_2 $MeNH_2$	90	95.3	90	20.17	18.55	12.16	C2/c
MOF-11 Cu_2(ATC)	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.47 mmol H_2ATC 0.22 mmol	H_2O	90	93.86	90	12.987	11.22	11.336	C2/c
MOF-11 Cu_2(ATC) dehydr.			90	90	90	8.4671	8.4671	14.44	P42/mmc
MOF-14 Cu_3 (BTB)	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.28 mmol H_3BTB 0.052 mmol	H_2O DMF EtOH	90	90	90	26.946	26.946	26.946	Im-3
MOF-32 Cd(ATC)	$Cd(NO_3)_2 \cdot 4H_2O$ 0.24 mmol H_4ATC 0.10 mmol	H_2O NaOH	90	90	90	13.468	13.468	13.468	P(-4)3m
MOF-33 Zn_2 (ATB)	$ZnCl_2$ 0.15 mmol H_4ATB 0.02 mmol	H_2O DMF EtOH	90	90	90	19.561	15.255	23.404	Imma

MOF-34 Ni(ATC)	$Ni(NO_3)_2$•$6H_2O$ 0.24 mmol H_4ATC 0.10 mmol	H_2O NaOH	90	90	90	10.066	11.163	19.201	$P2_12_12_1$
MOF-36 Zn_2 (MTB)	$Zn(NO_3)_2$•$4H_2O$ 0.20 mmol H_4MTB 0.04 mmol	H_2O DMF	90	90	90	15.745	16.907	18.167	Pbca
MOF-39 Zn_3O(HBTB)	$Zn(NO_3)_2$ $4H_2O$ 0.27 mmol H_3BTB 0.07 mmol	H_2O DMF EtOH	90	90	90	17.158	21.591	25.308	Pnma
MOF-n	Constituents Molar ratio M+L	Solvents	α	β	γ	a	b	c	Space group
NO305	$FeCl_2$•$4H_2O$ 5.03 mmol formic acid 86.90 mmol	DMF	90	90	120	8.2692	8.2692	63.566	R-3c
NO306A	$FeCl_2$•$4H_2O$ 5.03 mmol formic acid 86.90 mmol	DEF	90	90	90	9.9364	18.374	18.374	Pbcn
NO29 MOF-0 similar	$Mn(Ac)_2$•$4H_2O$ 0.46 mmol H_3BTC 0.69 mmol	DMF	120	90	90	14.16	33.521	33.521	P-1
BPR48 A2	$Zn(NO_3)_2$ $6H_2O$ 0.012 mmol H_2BDC 0.012 mmol	DMSO toluene	90	90	90	14.5	17.04	18.02	Pbca
BPR69 B1	$Cd(NO_3)_2$ $4H_2O$ 0.0212 mmol H_2BDC 0.0428 mmol	DMSO	90	98.76	90	14.16	15.72	17.66	Cc
BPR92 A2	$Co(NO_3)_2 \cdot 6H_2O$ 0.018 mmol H_2BDC 0.018 mmol	NMP	106.3	107.63	107.2	7.5308	10.942	11.025	P1
BPR95 C5	$Cd(NO_3)_2$ $4H_2O$ 0.012 mmol H_2BDC 0.36 mmol	NMP	90	112.8	90	14.460	11.085	15.829	P2(1)/n
Cu $C_6H_4O_6$	$Cu(NO_3)_2$•$2.5H_2O$ 0.370 mmol $H_2BDC(OH)_2$ 0.37 mmol	DMF chlorobenzene	90	105.29	90	15.259	14.816	14.13	P2(1)/c
M(BTC) MOF-0 similar	$Co(SO_4)$ H_2O 0.055 mmol H_3BTC 0.037 mmol	DMF	as for MOF-0						

MOF-n	Constituents Molar ratio M+L	Solvents	α	β	γ	a	b	c	Space group
Tb($C_6H_4O_6$)	$Tb(NO_3)_3•5H_2O$ 0.370 mmol $H_2(C_6H_4O_6)$ 0.56 mmol	DMF chlorobenzene	104.6	107.9	97.147	10.491	10.981	12.541	P-1
Zn (C_2O_4)	$ZnCl_2$ 0.370 mmol oxalic acid 0.37 mmol	DMF chlorobenzene	90	120	90	9.4168	9.4168	8.464	P(-3)1m
Co(CHO)	$Co(NO_3)_2•5H_2O$ 0.043 mmol formic acid 1.60 mmol	DMF	90	91.32	90	11.328	10.049	14.854	P2(1)/n
Cd(CHO)	$Cd(NO_3)_2•4H_2O$ 0.185 mmol formic acid 0.185 mmol	DMF	90	120	90	8.5168	8.5168	22.674	R-3c
Cu($C_3H_2O_4$)	$Cu(NO_3)_2•2.5H_2O$ 0.043 mmol malonic acid 0.192 mmol	DMF	90	90	90	8.366	8.366	11.919	P43
Zn_6 $(NDC)_5$ MOF-48	$Zn(NO_3)_2•6H_2O$ 0.097 mmol 14 NDC 0.069 mmol	DMF chlorobenzene H_2O_2	90	95.902	90	19.504	16.482	14.64	C2/m
MOF-47	$Zn(NO_3)_2$ $6H_2O$ 0.185 mmol $H_2(BDC[CH_3]_4)$ 0.185 mmol	DMF chlorobenzene H_2O_2	90	92.55	90	11.303	16.029	17.535	P2(1)/c
MO25	$Cu(NO_3)_2•2.5H_2O$ 0.084 mmol BPhDC 0.085 mmol	DMF	90	112.0	90	23.880	16.834	18.389	P2(1)/c

MOF-n	Constituents Molar ratio M+L	Solvents	α	β	γ	a	b	c	Space group
Cu-Thio	$Cu(NO_3)_2•2.5H_2O$ 0.084 mmol thiophene-dicarboxylic acid 0.085 mmol	DEF	90	113.6	90	15.4747	14.514	14.032	P2(1)/c
ClBDC1	$Cu(NO_3)_2•2.5H_2O$ 0.084 mmol $H_2(BDCCl_2)$ 0.085 mmol	DMF	90	105.6	90	14.911	15.622	18.413	C2/c

MOF-101	$Cu(NO_3)_2 \bullet 2.5H_2O$ 0.084 mmol BrBDC 0.085 mmol	DMF	90	90	90	21.607	20.607	20.073	Fm3m
$Zn_3(BTC)_2$	$ZnCl_2$ 0.033 mmol H_3BTC 0.033 mmol	DMF EtOH base added	90	90	90	26.572	26.572	26.572	Fm-3m
MOF-j	$Co(CH_3CO_2)_2 \bullet 4H_2O$ (1.65 mmol) $H_3(BZC)$ (0.95 mmol)	H_2O	90	112.0	90	17.482	12.963	6.559	C2
MOF-n	$Zn(NO_3)_2 \bullet 6H_2O$ H_3 (BTC)	ethanol	90	90	120	16.711	16.711	14.189	P6(3)/mcm
PbBDC	$Pb(NO_3)_2$ (0.181 mmol) $H_2(BDC)$ (0.181 mmol)	DMF ethanol	90	102.7	90	8.3639	17.991	9.9617	P2(1)/n
Znhex	$Zn(NO_3)_2 \bullet 6H_2O$ (0.171 mmol) H_3BTB (0.114 mmol)	DMF p-xylene ethanol	90	90	120	37.1165	37.117	30.019	P3(1)c

MOF-n	Constituents Molar ratio M+L	Solvents	α	β	γ	a	b	c	Space group
AS16	$FeBr_2$ 0.927 mmol $H_2(BDC)$ 0.927 mmol	DMF anhydr.	90	90.13	90	7.2595	8.7894	19.484	P2(1)c
AS27-2	$FeBr_2$ 0.927 mmol $H_3(BDC)$ 0.464 mmol	DMF anhydr.	90	90	90	26.735	26.735	26.735	Fm3m
AS32	$FeCl_3$ 1.23 mmol $H_2(BDC)$ 1.23 mmol	DMF anhydr. ethanol	90	90	120	12.535	12.535	18.479	P6(2)c
AS54-3	$FeBr_2$ 0.927 BPDC 0.927 mmol	DMF anhydr. n-propanol	90	109.98	90	12.019	15.286	14.399	C2
AS61-4	$FeBr_2$ 0.927 mmol m-BDC 0.927 mmol	pyridine anhydr.	90	90	120	13.017	13.017	14.896	P6(2)c
AS68-7	$FeBr_2$ 0.927 mmol m-BDC 1.204 mmol	DMF anhydr. pyridine	90	90	90	18.3407	10.036	18.039	$Pca2_1$

Zn(ADC)	$Zn(NO_3)_2 \cdot 6H_2O$ 0.37 mmol H_2(ADC) 0.36 mmol	DMF chlorobenzene	90	99.85	90	16.764	9.349	9.635	C2/c
MOF-12 Zn_2 (ATC)	$Zn(NO_3)_2 \cdot 6H_2O$ 0.30 mmol H_4(ATC) 0.15 mmol	ethanol	90	90	90	15.745	16.907	18.167	Pbca
MOF-20 ZnNDC	$Zn(NO_3)_2 \cdot 6H_2O$ 0.37 mmol H_2NDC 0.36 mmol	DMF chlorobenzene	90	92.13	90	8.13	16.444	12.807	P2(1)/c

MOF-n	Constituents Molar ratio M+L	Solvents	α	β	γ	a	b	c	Space group
MOF-37	$Zn(NO_3)_2 \cdot 6H_2O$ 0.20 mmol H_2NDC 0.20 mmol	DEF chlorobenzene	72.38	83.16	84.33	9.952	11.576	15.556	P-1
Zn(NDC) (DMSO)	$Zn(NO_3)_2 \cdot 6H_2O$ H_2NDC	DMSO	68.08	75.33	88.31	8.631	10.207	13.114	P-1
Zn(NDC)	$Zn(NO_3)_2 \cdot 6H_2O$ H_2NDC		90	99.2	90	19.289	17.628	15.052	C2/c
Zn(HPDC)	$Zn(NO_3)_2 \cdot 4H_2O$ 0.23 mmol H_2(HPDC) 0.05 mmol	DMF H_2O	107.9	105.06	94.4	8.326	12.085	13.767	P-1
Co(HPDC)	$Co(NO_3)_2 \cdot 6H_2O$ 0.21 mmol H_2 (HPDC) 0.06 mmol	DMF H_2O/ ethanol	90	97.69	90	29.677	9.63	7.981	C2/c
Zn_3(PDC)2.5	$Zn(NO_3)_2 \cdot 4H_2O$ 0.17 mmol H_2(HPDC) 0.05 mmol	DMF/ ClBz H20/ TEA	79.34	80.8	85.83	8.564	14.046	26.428	P-1
Cd_2 (TPDC)2	$Cd(NO_3)_2 \cdot 4H_2O$ 0.06 mmol H_2(HPDC) 0.06 mmol	methanol/ CHP H_2O	70.59	72.75	87.14	10.102	14.412	14.964	P-1
Tb(PDC) 1.5	$Tb(NO_3)_3 \cdot 5H_2O$ 0.21 mmol H_2(PDC) 0.034 mmol	DMF H_2O/ ethanol	109.8	103.61	100.14	9.829	12.11	14.628	P-1
ZnDBP	$Zn(NO_3)_2 \cdot 6H_2O$ 0.05 mmol dibenzyl phosphate 0.10 mmol	MeOH	90	93.67	90	9.254	10.762	27.93	P2/n
Zn_3(BPDC)	$ZnBr_2$ 0.021 mmol 4,4‘BPDC 0.005 mmol	DMF	90	102.76	90	11.49	14.79	19.18	P21/n

MOF-n	Constituents Molar ratio M+L	Sol-vents	α	β	γ	a	b	c	Space group
CdBDC	$Cd(NO_3)_2\cdot4H_2O$ 0.100 mmol $H_2(BDC)$ 0.401 mmol	DMF Na_2SiO_3 (aq)	90	95.85	90	11.2	11.11	16.71	P21/n
Cd-mBDC	$Cd(NO_3)_2\cdot4H_2O$ 0.009 mmol $H_2(mBDC)$ 0.018 mmol	DMF $MeNH_2$	90	101.1	90	13.69	18.25	14.91	C2/c
Zn_4OBNDC	$Zn(NO_3)_2\cdot6H_2O$ 0.041 mmol BNDC	DEF $MeNH_2$ H_2O_2	90	90	90	22.35	26.05	59.56	Fmmm
Eu(TCA)	$Eu(NO_3)_3\cdot6H_2O$ 0.14 mmol TCA 0.026 mmol	DMF chlorobenzene	90	90	90	23.325	23.325	23.325	Pm-3n
Tb(TCA)	$Tb(NO_3)_3\cdot6H_2O$ 0.069 mmol TCA 0.026 mmol	DMF chlorobenzene	90	90	90	23.272	23.272	23.372	Pm-3n
Formates	$Ce(NO_3)_3\cdot6H_2O$ 0.138 mmol formic acid 0.43 mmol	H_2O ethanol	90	90	120	10.668	10.667	4.107	R-3m
	$FeCl_2\cdot4H_2O$ 5.03 mmol formic acid 86.90 mmol	DMF	90	90	120	8.2692	8.2692	63.566	R-3c
	$FeCl_2\cdot4H_2O$ 5.03 mmol formic acid 86.90 mmol	DEF	90	90	90	9.9364	18.374	18.374	Pbcn
	$FeCl_2\cdot4H_2O$ 5.03 mmol formic acid 86.90 mmol	DEF	90	90	90	8.335	8.335	13.34	P-31c
NO330	$FeCl_2\cdot4H_2O$ 0.50 mmol formic acid 8.69 mmol	formamide	90	90	90	8.7749	11.655	8.3297	Pnna
NO332	$FeCl_2\cdot4H_2O$ 0.50 mmol formic acid 8.69 mmol	DIP	90	90	90	10.0313	18.808	18.355	Pbcn

NO333	$FeCl_2 \cdot 4H_2O$ 0.50 mmol formic acid 8.69 mmol	DBF	90	90	90	45.2754	23.861	12.441	Cmcm
NO335	$FeCl_2 \cdot 4H_2O$ 0.50 mmol formic acid 8.69 mmol	CHF	90	91.372	90	11.5964	10.187	14.945	P21/n
NO336	$FeCl_2 \cdot 4H_2O$ 0.50 mmol formic acid 8.69 mmol	MFA	90	90	90	11.7945	48.843	8.4136	Pbcm
NO13	$Mn(Ac)_2 \cdot 4H_2O$ 0.46 mmol benzoic acid 0.92 mmol bipyridine 0.46 mmol	ethanol	90	90	90	18.66	11.762	9.418	Pbcn
NO29 MOF-0 similar	$Mn(Ac)_2 \cdot 4H_2O$ 0.46 mmol H_3BTC 0.69 mmol	DMF	120	90	90	14.16	33.521	33.521	P-1
$Mn(hfac)_2(O_2CC_6H_5)$	$Mn(Ac)_2 \cdot 4H_2O$ 0.46 mmol Hfac 0.92 mmol bipyridine 0.46 mmol	ether	90	95.32	90	9.572	17.162	14.041	C2/c
BPR43G2	$Zn(NO_3)_2 \cdot 6H_2O$ 0.0288 mmol H_2BDC 0.0072 mmol	DMF CH_3CN	90	91.37	90	17.96	6.38	7.19	C2/c

MOF-n	Constituents Molar ratio M+L	Sol-vents	α	β	γ	a	b	c	Space group
BPR48A2	$Zn(NO_3)_2\ 6H_2O$ 0.012 mmol H_2BDC 0.012 mmol	DMSO toluene	90	90	90	14.5	17.04	18.02	Pbca
BPR49B1	$Zn(NO_3)_2\ 6H_2O$ 0.024 mmol H_2BDC 0.048 mmol	DMSO methanol	90	91.172	90	33.181	9.824	17.884	C2/c
BPR56E1	$Zn(NO_3)_2\ 6H_2O$ 0.012 mmol H_2BDC 0.024 mmol	DMSO n-propanol	90	90.096	90	14.5873	14.153	17.183	P2(1)/n
BPR68D10	$Zn(NO_3)_2\ 6H_2O$ 0.0016 mmol H_3BTC 0.0064 mmol	DMSO benzene	90	95.316	90	10.0627	10.17	16.413	P2(1)/c

BPR69B1	$Cd(NO_3)_2\ 4H_2O$ 0.0212 mmol H_2BDC 0.0428 mmol	DMSO	90	98.76	90	14.16	15.72	17.66	Cc
BPR73E4	$Cd(NO_3)_2\ 4H_2O$ 0.006 mmol H_2BDC 0.003 mmol	DMSO toluene	90	92.324	90	8.7231	7.0568	18.438	P2(1)/n
BPR76D5	$Zn(NO_3)_2\ 6H_2O$ 0.0009 mmol H_2BzPDC 0.0036 mmol	DMSO	90	104.17	90	14.4191	6.2599	7.0611	Pc
BPR80B5	$Cd(NO_3)_2{\bullet}4H_2O$ 0.018 mmol H_2BDC 0.036 mmol	DMF	90	115.11	90	28.049	9.184	17.837	C2/c
BPR80H5	$Cd(NO_3)_2\ 4H_2O$ 0.027 mmol H_2BDC 0.027 mmol	DMF	90	119.06	90	11.4746	6.2151	17.268	P2/c

MOF-n	Constituents Molar ratio M+L	Sol-vents	α	β	γ	a	b	c	Space group
BPR82C6	$Cd(NO_3)_2\ 4H_2O$ 0.0068 mmol H_2BDC 0.202 mmol	DMF	90	90	90	9.7721	21.142	27.77	Fdd2
BPR86C3	$Co(NO_3)_2\ 6H_2O$ 0.0025 mmol H_2BDC 0.075 mmol	DMF	90	90	90	18.3449	10.031	17.983	Pca2(1)
BPR86H6	$Cd(NO_3)_2{\cdot}6H_2O$ 0.010 mmol H_2BDC 0.010 mmol	DMF	80.98	89.69	83.412	9.8752	10.263	15.362	P-1
	$Co(NO_3)_2\ 6H_2O$	NMP	106.3	107.63	107.2	7.5308	10.942	11.025	P1
BPR95A2	$Zn(NO_3)_2\ 6H_2O$ 0.012 mmol H_2BDC 0.012 mmol	NMP	90	102.9	90	7.4502	13.767	12.713	P2(1)/c
$CuC_6F_4O_4$	$Cu(NO_3)_2{\bullet}2.5H_2O$ 0.370 mmol $H_2BDC(OH)_2$ 0.37 mmol	DMF chloro-benzene	90	98.834	90	10.9675	24.43	22.553	P2(1)/n
Fe Formic	$FeCl_2{\bullet}4H_2O$ 0.370 mmol formic acid 0.37 mmol	DMF	90	91.543	90	11.495	9.963	14.48	P2(1)/n

Mg Formic	$Mg(NO_3)_2 \cdot 6H_2O$ 0.370 mmol formic acid 0.37 mmol	DMF	90	91.359	90	11.383	9.932	14.656	P2(1)/n
$MgC_6H_4O_6$	$Mg(NO_3)_2 \cdot 6H_2O$ 0.370 mmol $H_2BDC(OH)_2$ 0.37 mmol	DMF	90	96.624	90	17.245	9.943	9.273	C2/c
Zn C_2H_4BDC MOF-38	$ZnCl_2$ 0.44 mmol CBBDC 0.261 mmol	DMF	90	94.714	90	7.3386	16.834	12.52	P2(1)/n

MOF-n	Constituents Molar ratio M+L	Solvents	α	β	γ	a	b	c	Space group
MOF-49	$ZnCl_2$ 0.44 mmol m-BDC 0.261 mmol	DMF CH_3CN	90	93.459	90	13.509	11.984	27.039	P2/c
MOF-26	$Cu(NO_3)_2 \cdot 5H_2O$ 0.084 mmol DCPE 0.085 mmol	DMF	90	95.607	90	20.8797	16.017	26.176	P2(1)/n
MOF-112	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.084 mmol *o*-Br-*m*-BDC 0.085 mmol	DMF ethanol	90	107.49	90	29.3241	21.297	18.069	C2/c
MOF-109	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.084 mmol KDB 0.085 mmol	DMF	90	111.98	90	23.8801	16.834	18.389	P2(1)/c
MOF-111	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.084 mmol o-BrBDC 0.085 mmol	DMF ethanol	90	102.16	90	10.6767	18.781	21.052	C2/c
MOF-110	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.084 mmol thiophene-dicarboxylic acid 0.085 mmol	DMF	90	90	120	20.0652	20.065	20.747	R-3/m
MOF-107	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.084 mmol thiophene-dicarboxylic acid 0.085 mmol	DEF	104.8	97.075	95.206	11.032	18.067	18.452	P-1

MOF-n	Constituents Molar ratio M+L	Sol-vents	α	β	γ	a	b	c	Space group
MOF-108	Cu(NO3)2•2.5H2O 0.084 mmol thiophene-dicarboxylic acid 0.085 mmol	DBF/ methanol	90	113.63	90	15.4747	14.514	14.032	C2/c
MOF-102	Cu(NO3)2•2.5H2O 0.084 mmol H2(BDCCl2) 0.085 mmol	DMF	91.63	106.24	112.01	9.3845	10.794	10.831	P-1
Clbdc1	Cu(NO3)2•2.5H2O 0.084 mmol H2(BDCCl2) 0.085 mmol	DEF	90	105.56	90	14.911	15.622	18.413	P-1
Cu(NMOP)	Cu(NO3)2•2.5H2O 0.084 mmol NBDC 0.085 mmol	DMF	90	102.37	90	14.9238	18.727	15.529	P2(1)/m
Tb(BTC)	Tb(NO3)3•5H2O 0.033 mmol H3BTC 0.033 mmol	DMF	90	106.02	90	18.6986	11.368	19.721	
Zn3(BTC)2 Honk	ZnCl2 0.033 mmol H3BTC 0.033 mmol	DMF ethanol	90	90	90	26.572	26.572	26.572	Fm-3m
Zn4O(NDC)	Zn(NO3)2•4H2O 0.066 mmol 14NDC 0.066 mmol	DMF ethanol	90	90	90	41.5594	18.818	17.574	aba2
IRMOF-2	Zn(NO3)2•4H2O 0.160 mmol o-Br-BDC 0.60 mmol	DEF	90	90	90	25.772	25.772	25.772	Fm-3m
IRMOF-3	Zn(NO3)2•4H2O 0.20 mmol H2N-BDC 0.60 mmol	DEF ethanol	90	90	90	25.747	25.747	25.747	Fm-3m
IRMOF-4	Zn(NO3)2•4H2O 0.11 mmol [C3H7O]2-BDC 0.48 mmol	DEF	90	90	90	25.849	25.849	25.849	Fm-3m

IRMOF-5	Zn(NO3)2•4H2O 0.13 mmol [C5H11O]2-BDC 0.50 mmol	DEF	90	90	90	12.882	12.882	12.882	Pm-3m
IRMOF-6	Zn(NO3)2•4H2O 0.20 mmol [C2H4]-BDC 0.60 mmol	DEF	90	90	90	25.842	25.842	25.842	Fm-3m
IRMOF-7	Zn(NO3)2•4H2O 0.07 mmol 1,4NDC 0.20 mmol	DEF	90	90	90	12.914	12.914	12.914	Pm-3m
IRMOF-8	Zn(NO3)2•4H2O 0.55 mmol 2,6NDC 0.42 mmol	DEF	90	90	90	30.092	30.092	30.092	Fm-3m
IRMOF-9	Zn(NO3)2•4H2O 0.05 mmol BPDC 0.42 mmol	DEF	90	90	90	17.147	23.322	25.255	Pnnm
IRMOF-10	Zn(NO3)2•4H2O 0.02 mmol BPDC 0.012 mmol	DEF	90	90	90	34.281	34.281	34.281	Fm-3m
IRMOF-11	Zn(NO3)2•4H2O 0.05 mmol HPDC 0.20 mmol	DEF	90	90	90	24.822	24.822	56.734	R-3m

MOF-n	Constituents Molar ratio M+L	Sol-vents	α	β	γ	a	b	c	Space group
IRMOF-12	Zn(NO3)2•4H2O 0.017 mmol HPDC 0.12 mmol	DEF	90	90	90	34.281	34.281	34.281	Fm-3m
IRMOF-13	$Zn(NO_3)_2 \cdot 4H_2O$ 0.048 mmol PDC 0.31 mmol	DEF	90	90	90	24.822	24.822	56.734	R-3m
IRMOF-14	$Zn(NO_3)_2 \cdot 4H_2O$ 0.17 mmol PDC 0.12 mmol	DEF	90	90	90	34.381	34.381	34.381	Fm-3m
IRMOF-15	$Zn(NO_3)_2 \cdot 4H_2O$ 0.063 mmol TPDC 0.025 mmol	DEF	90	90	90	21.459	21.459	21.459	Im-3m
IRMOF-16	$Zn(NO_3)_2 \cdot 4H_2O$ 0.0126 mmol TPDC 0.05 mmol	DEF NMP	90	90	90	21.49	21.49	21.49	Pm-3m

ADC	Acetylenedicarboxylic acid
NDC	Naphthalenedicarboxylic acid
BDC	Benzenedicarboxylic acid
ATC	Adamantanetetracarboxylic acid
BTC	Benzenetricarboxylic acid
BTB	Benzenetribenzoic acid
MTB	Methanetetrabenzoic acid
ATB	Adamantanetetrabenzoic acid
ADB	Adamantanedibenzoic acid

Further metal-organic frameworks are MOF-2 to 4, MOF-9, MOF-31 to 36, MOF-39, MOF-69 to 80, MOF103 to 106, MOF-122, MOF-125, MOF-150, MOF-177, MOF-178, MOF-235, MOF-236, MOF-500, MOF-501, MOF-502, MOF-505, IRMOF-1, IRMOF-61, IRMOP-13, IRMOP-51, MIL-17, MIL-45, MIL-47, MIL-53, MIL-59, MIL-60, MIL-61, MIL-63, MIL-68, MIL-79, MIL-80, MIL-83, MIL-85, CPL-1 to 2, SZL-1, which are described in the literature.

Particularly preferred metal-organic frameworks are MIL-53, Zn-tBu-isophthalic acid, Al-BDC, MOF-5, MOF-177, MOF-505, IRMOF-8, IRMOF-11, Cu-BTC, Al-NDC, Al-aminoBDC, Cu-BDC-TEDA, Zn-BDC-TEDA, Al-BTC, Cu-BTC, Al-NDC, Mg-NDC, Al-fumarate, Zn-2-aminoimidazolate, Cu-biphenyldicarboxylate-TEDA, MOF-74, Cu-BPP, Sc-terephthalate. Greater preference is given to Sc-terephthalate, Al-BDC and Al-BTC.

Even more preferred metal-organic framework materials are Zn-BTB, Mg-2,6-dihydroxy-terephthalate, Al-fumarate and Cu-1,3,5-BTC, especially Zn-BTB, Al-fumarate, Cu-1,3,5-BTC.

Apart from the conventional method of preparing the MOFs, as described, for example, in US 5,648,508, they can also be prepared by an electrochemical route. In this regard, reference is made to DE-A 103 55 087 and WO-A 2005/049892. The metal-organic frameworks prepared in this way have particularly good properties in respect of the adsorption and desorption of chemical substances, in particular gases.

Regardless of the method of preparation, the metal-organic framework is obtained in pulverulent or crystalline form. It is preferably used as loose material. The metal-organic framework can also be converted into a shaped body.

Accordingly, in a preferred embodiment, the metal-organic framework material is used in step (a) in form of shaped bodies. Preferably, before step (a) the shaped bodies are crushed.

Preferred processes for shaping are extrusion or tableting. In the production of shaped bodies, further materials such as binders, lubricants or other additives can be added to the metal-organic framework. It is likewise conceivable to produce mixtures of framework and other adsorbents such as activated carbon as shaped bodies or for them to form separate shaped bodies which are then used as mixtures of shaped bodies.

According to the present invention these further materials, like graphite, can be easily separated by means known in the art, like filtration, when the organic compound and optionally the metal ion are in solved form.

The possible geometries of these shaped bodies are in principle not subject to any restrictions. For example, possible shapes are, inter alia, pellets such as disk-shaped pellets, pills, spheres, granules, extrudates such as rods, honeycombs, grids or hollow bodies.

The metal-organic framework is preferably present as crushed shaped bodies. Preferred embodiments are tablets and elongated extrudates. Methods for crushing are known in the ar. Crushing can be obtained, e.g., via malt milling, ball milling, applying mechanical force by wheeling, sonification or the like.

The shaped bodies -before crushing- preferably have a dimension in one direction in space in the range from 0.2 mm to 30 mm, more preferably from 0.5 mm to 5 mm, in particular from 1 mm to 3 mm.

To produce the shaped bodies, it is in principle possible to employ all suitable methods. In particular, the following processes are preferred:

- Kneading of the framework either alone or together with at least one binder and/or at least one pasting agent and/or at least one template compound to give a mixture; shaping of the resulting mixture by means of at least one suitable method such as extrusion; optionally washing and/or drying and/or calcination of the extrudate; optionally finishing treatment.
- Application of the framework to at least one optionally porous support material. The material obtained can then be processed further by the above-described method to give a shaped body.
- Application of the framework to at least one optionally porous substrate.

Kneading 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), whose relevant contents are fully incorporated by reference into the present patent application.

For example, the kneading and/or shaping can be carried out by means of a piston press, roller press in the presence or absence of at least one binder, compounding, pelletization, tableting, extrusion, coextrusion, foaming, spinning, coating, granulation, preferably spray granulation, spraying, spray drying or a combination of two or more of these methods.

Very particular preference is given to producing pellets and/or tablets.

The kneading and/or shaping 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.

The kneading and/or shaping is, in a further embodiment, carried out with addition of at least one binder, with the binder used basically being able to be any chemical compound which ensures the desired viscosity for the kneading and/or shaping of the composition to be kneaded and/or shaped. Accordingly, binders can, for the purposes of the present invention, be either viscosity-increasing or viscosity-reducing compounds.

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 described, for example, in JP 03-037156 A, for example montmorillonite, kaolin, bentonite, hallosite, dickite, nacrite and anauxite, alkoxysilanes as 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, tributoxyzirconate, silica sols, amphiphilic substances and/or graphites. Particular preference is given to graphite.

As viscosity-increasing compound, it is, for example, also possible to use, if appropriate in addition to the abovementioned compounds, an organic compound and/or a hydrophilic polymer such as cellulose or a cellulose derivative such as methylcellulose and/or a polyacrylate and/or a polymethacrylate and/or a polyvinyl alcohol and/or a polyvinylpyrrolidone and/or a polyisobutene and/or a polytetrahydrofuran.

As pasting agent, it is possible to use, inter alia, preferably water or at least one alcohol such as 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.

Further additives which can be used for kneading and/or shaping 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.

The order of the additives such as template compound, binder, pasting agent, viscosity-increasing substance during shaping and kneading is in principle not critical.

In a further, preferred embodiment, the shaped body obtained by kneading and/or shaping is subjected to at least one drying step which is generally carried out at a temperature in the range from 25 to 300°C, preferably in the range from 50 to 300°C and particularly preferably in the range from 100 to 300°C. It is likewise possible to carry out drying under reduced pressure or under a protective gas atmosphere or by spray drying.

In a particularly preferred embodiment, at least one of the compounds added as additives is at least partly removed from the shaped body during this drying process.

Accordingly, in case of shaped bodies (irrespective whether or not crushed) are used it is possible that also additives from the shaping process are comprised. When using an alkaline liquid in step (a) these additives can be separated off in step (b) when they are not solvable. Thus, alkaline solution is preferred in step (a). In case the additives are soluble in acids then the acidic solution is preferred.

However according to the present invention the total amount of additives in a shaped body (crushed or uncrushed) should be low and preferably at most 25 weight-% (even more preferably 10%, even more preferably 5%, even more preferably 3%) based on the total weight of the shaped body. Also the number of different additives should be low, preferably only 5 or less (preferably only 3 or less, even more preferably only 2 or less). As a particular additive, graphite should be mentioned.

In step (a) the metal-organic framework material is treated with an acidic or alkaline liquid. Preferably, the liquid is an aqueous liquid. According to the invention the term “aqueous” encompasses water and mixtures of water with miscible liquids, like alcohols, for example ethanol, methanol or the like. The mixture contains preferably at least 50 % (V/V), more preferably 75 %, more preferably 90 % and even more preferably is the liquid water.

The liquid used in step (a) can be an acidic liquid. In such a case the preferred pH of said liquid is a pH of less than 4, more preferably, less than 3, even more preferably less than 2, even more preferably the pH is 1 or lower. When the liquid is an acidic liquid then the at least bidentate organic compound is preferably isolated from the solid residue obtained in step (b).

The pH can be adjusted by adding common inorganic acids, like hydrochloric acid, sulfuric acid, nitric acid.

In step (a) the liquid can be an alkaline liquid, which is preferred. Then the alkaline liquid preferably has a pH of more than 10, more preferably more than 11, even more than 12 and even more than 13. The pH can be adjusted by adding common inorganic bases, like sodium hydroxide, potassium hydroxide, ammonia.

It is preferred that an alkaline liquid is used.

The at least bidentate organic compound can be isolated in step (c) from the liquid, optionally after acidification. Methods for separating off the at least bidentate organic compound after acidification are known in the art.

It is possible that the at least one metal ion is also recovered. Methods for the isolation of the metal ion are known in the art. If an alkaline solution is used, the optional step (b) is mandatory so that the metal ion is comprised or consists of the solid residue. Further purification steps can follow. If an acidic solution is used step (c) results in the isolation of the organic compound and a solution containing the metal ion. The following isolation of the metal ion can then be carried out by methods known in the art, like precipitation reactions, ion exchange, or the like.

Preferably, in step (a) the metal-organic framework material is treated with the acidic or alkaline liquid by contacting the material with the liquid and mixing, like be means of agitating.

Preferably, step (a) is carried out at room temperature. It is clear to the practitioner in the art that also higher temperatures can be used.

Examples:

Example 1: Basolite Z377 (MOF-177, Zn-BTB)

1.1. Synthesis Basolite Z377 according to following example:
Under a nitrogen atmosphere 216 g $Zn(NO_3)_2 \times 6 H_2O$ was dissolved in 6 l dietylformamide (DEF). Under stirring 60 g 1,3,5-Tri-(4-carboxyphenyl)-benzene (BTB) was added. The resulting solution was heated up to 100°C without stirring and kept at this temperature for 24 h. After cooling down to room temperature the obtained crystals were separated from the mother liquor, washed 4 times with 0.90 l Diethylformamide (60°C) and 10 times with 0.9 l chloroform (50°C). The obtained yellow crystals were dried for 3h at room temperature at 20 mbar. Further activation was performed at full vacuum rising the temperature slowly to 130°C until no loss on drying was observable anymore. 58.9 g of Zn-MOF could be isolated (75% yield on BTB). The Langmuir surface area was found to be 4627 m^2/g.

1.2. Recycling procedure employing NaOH and HCl:
In a beaker containing 500 ml of distilled water 20.0 g caustic soda (NaOH, 500 mmol) was dissolved. Under stirring 57.4 g Basolite Z377 (Zn-BTB-MOF, 50 mmol) of example 1.1 was added (pH 13.21). After stirring for 1h at room temperature not dissolved solid material was separated

by filtration. The filter cake was washed three times with 50 ml distilled water. The obtained filter cake (No-1) was dried at 120°C for 16 h giving 14.5 g of a white solid. The carbon content by elemental analysis was 1.2 g/100 g. The recovered yield on Zinc was 72%.

The pH of the combined filtrate was brought to acidic conditions (pH =1) by adding 65.16 g hydrochloric acid (32%, 571 mmol) and stirred for 30 min to precipitate the BTB linker. The precipitate was isolated via filtration, and washed with in total 2 l of distilled water. The obtained filter cake (No-2) was dried at 120°C for 16 h giving 39.1 g of a yellow solid. The elemental analysis revealed only traces of impurities: Zn 0.005%; Na 0.033%; Cl 0.05%. The carbon content was found to be 70.5 g/100 g. The recovered yield on BTB was 89%. NMR analysis revealed high purity. The BTB material could be used in a procedure for new MOF-177 preparation as given in example 1.1 with comparable characteristics.

^{1}H-NMR (DMSO-d_6, 500.13 MHz): δ = 13.04 (s, 3 H), 8.08 (m, 12 H).
^{13}C-NMR (DMSO-d_6, 125.77 MHz): δ = 167.18, 143.79, 140.68, 129.92, 129.91, 127.53, 127.34, 125.50.

1.3. Synthesis of Basolite Z377 employing BTB from example 1.2

Under a nitrogen atmosphere 64.8 g $Zn(NO_3)_2$ x 6 H_2O (Sigma-Aldrich, 22,873-7) was dissolved in 1800 ml DEF. Under stirring 18.0 g 1,3,5-Tri-(4-carboxyphenyl)-benzene (BTB) from example 1.2 was added (pH 3.94). The resulting solution was heated up to 100°C without stirring and kept at this temperature for 24 h. After cooling down to room temperature the obtained crystals were separated from the mother liquor, washed 4 times with 0.25 l Diethylformamide and extracted with hot chloroform for 16 h in a Soxhlett extractor. The obtained yellow crystals were dried for 3h at room temperature at 20 mbar. Further activation was performed at full vacuum rising the temperature slowly to 130°C until no loss on drying was observable anymore. 20.94 g of Zn-MOF could be isolated (88.9% yield on BTB) with a tamped density of 220 g/l. The Langmuir surface area was found to be 4509 m²/g and the hydrogen uptake at 77 K at 1 bar to be 142.2 ccm/g.

1.4. Recycling procedure employing HCl:

In a beaker 11.48 g Basolite Z377 (10 mmol) from example 1.1 is suspended in 100 ml of distilled water (pH 6.77) at room temperature. Under stirring pH is adjusted to pH = 1 and kept at this pH for 1 h via addition of 32% hydrochloric acid (in total 8.95 g). The precipitate is filtered of and washed wit 1 liter of distilled water. The obtained filter cake was dried at 120°C for 16 h giving 8.0 g of a white solid. The carbon content by elemental analysis was 71.6 g/100 g, the zinc content was 0.61 g/100 g. The recovered yield on BTB was 91.3%.

Example 2: Basolite A520 (Aluminum fumarate MOF) tablets

2.1. Synthesis Basolite A520 according to following example:

The material that was applied was prepared as described in WO-A 2012/042410. Its surface area ranged from 1200-1300 m²/g. Shaped bodies were prepared by thoroughly mixing the obtained Basolite A520 powder with 1.5 wt% of graphite for 0.05 h and subsequently shaping it to 3x3 mm tablets on a Korsch SP300 tableting press (filling height powder: 7.8 mm). The Langmuir surface area of the tablets was 1157 m^2/g, the lateral crush strength 19.2 N.

2.2. Recycling procedure employing NaOH and HCl:
In a beaker containing 150 ml of distilled water 12.0 g caustic soda (NaOH, 300 mmol) was dissolved. Under stirring 14.22 g crushed tablets of Basolite A520 (Al-Fumarate-MOF, 90 mmol) were added (pH 13.33). After stirring for 1h at room temperature not dissolved solid material was separated by filtration. The filter cake was washed three times with 20 ml distilled water. The obtained filter cake (No-1) was dried at 120°C for 16 h giving 0.01 g of a black solid (graphite additive of the tablets).

The pH of the combined filtrate was brought to acidic conditions (pH =1) by adding 63.4 g hydrochloric acid (32%, 556 mmol) and stirred for 30 min to precipitate the fumaric acid linker. The precipitate was isolated via filtration and then washed four times with each 25 ml of distilled water. The obtained filter cake (No-2) was dried at 120°C for 16 h giving 7.36 g of a white solid. The carbon content by elemental analysis was found to be 40.4 g/100 g, the aluminum content to be 0.9 g/100 g.

An ^1H and ^{13}C-NMR analysis revealed a high purity of the obtained fumaric acid linker. The recovered yield was 70.4 %.

^1H-NMR (DMSO-d_6, 500.13 MHz): δ = 12.99 (s, 2 H), 6.65 (s, 2 H).
^{13}C-NMR (DMSO-d_6, 125.77 MHz): δ = 166.3, 134.3, 133.7.

Example 3: Basolite C300 (HKUST-1)

3.1. Synthesis Basolite C300 according to following example:
The material was synthesized according to WO-A 2007/090809. Its surface area ranged from 1900-2100 m^2/g. Shaped bodies were prepared by thoroughly mixing the obtained Basolite C300 powder with 1.0 wt% of graphite for 0.05 h and subsequently shaping it to 3x3 mm tablets on a Horn tableting press. The Langmuir surface area of the tablets was 1409 m^2/g, the lateral crush strength 15 N.

3.2. Recycling procedure employing NaOH and HCl:
In a beaker containing 200 ml of distilled water 8.0 g caustic soda (NaOH, 200 mmol) was dissolved. Under stirring 12.1 g crushed tablets of Basolite C300 (Cu-BTC, 20 mmol) were added (pH 13.54). After stirring for 1h at room temperature not dissolved solid material was separated by filtration. The filter cake was washed three times with 20 ml distilled water. The obtained filter cake (No-1) was dried at 120°C for 16 h giving 4.32 g of a black solid (Mixture of copper hydroxide and graphite additive of the tablets). The carbon content by elemental analysis was 8.4 g/100 g.

The pH of the combined filtrate was brought to acidic conditions (pH =1) by adding 24.36 g hydrochloric acid (32%, 214 mmol) and stirred for 30 min to precipitate the BTC linker. The precipitate was isolated via filtration and then washed in total with 600 ml of distilled water. The obtained filter cake (No-2) was dried at 120°C for 16 h giving 4.76 g of a white solid. The carbon content by elemental analysis was found to be 51.4 g/100 g, the copper content to be less than 0.001 g/100 g.

An ^1H and ^{13}C-NMR analysis revealed a high purity of the obtained BTC linker. The recovered yield on BTC was 56.7 %.

^1H-NMR (DMSO-d_6, 500.13 MHz): δ = 13.00 (s, 3 H), 8.65 (s, 3 H).
^{13}C-NMR (DMSO-d_6, 125.77 MHz): δ = 165.9, 133.6, 131.8.

Claims

1. Process for the recovery of an at least bidentate organic compound comprised in a porous metal-organic framework material, the material comprising the at least bidentate organic compound coordinated to at least one metal ion, the process comprising the steps of
   (a) treating the metal-organic framework material with an acidic or alkaline liquid;
   (b) optionally separating off solid residue;
   (c) isolating the at least bidentate organic compound.

2. The process of claim 1, wherein in step (a) the liquid is an aqueous liquid.

3. The process of claim 1 or 2, wherein in step (a) the liquid is an acidic liquid.

4. The process of claim 3, wherein the acidic liquid has a pH of less than 4.

5. The process of any one of claims 1 to 4, wherein the liquid is an acidic liquid and the at least bidentate organic compound is isolated from the solid residue obtained in step (b).

6. The process of claim 1 or 2, wherein in step (a) the liquid is an alkaline liquid.

7. The process of claim 6, wherein the alkaline liquid has a pH of more than 10.

8. The process of any one of claims 1, 2, 6 or 7, wherein the at least bidentate organic compound is isolated in step (c) from the liquid, optionally after acidification.

9. The process of any one of claims 1 to 8, wherein also the at least one metal ion is recovered.

10. The process of any one of claims 1 to 9, wherein the metal-organic framework material used in step (a) is in form of crushed shaped bodies.

11. The process of any one of claims 1 to 10, wherein the at least bidentate organic compound is derived from a di- tri- or tetracarboxylic acid.

12. The process of any one of claims 1 to 11, wherein the at least bidentate organic compound is derived from an organic compound selected from the group consisting of 1,3,5-tri-(4-carboxyphenyl)-benzene, benzenetricarboxylic acid, dihydroxyterephthalic acid and fumaric acid.

13. The process of any one of claims 1 to 12, wherein the at least one metal ion is selected from the group metals consisting of Mg, Al, Li, Ca, Zr, Ti, V, Cr, Mo, Fe, Co, Cu, Ni, Zn, and La.

14. The process of any one of claims 1 to 13, wherein in step (a) the metal-organic framework material is treated with the acidic or alkaline liquid by contacting the material with the liquid and mixing.

15. The process of any one of claims 1 to 14, wherein step (a) is carried out at room temperature.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2014/064724

A. CLASSIFICATION OF SUBJECT MATTER

B01J 20/34(2006.01)i; B01D 11/02(2006.01)i; B01J 20/22(2006.01)i; B01J 20/282(2006.01)i

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)

B01J20/-; B01D11/-

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)

CNABS,SIPOABS,CNTXT,CNKI,DWPI,VEN,EPODOC,USTXT,JPTXT,ACS:recovery,reuse,bidentate,ligand,linker, chelation,metal-organic,framework,porous,adsorbent,treat,acidic,acid,alkaline

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2230288 A3 (BASF SE) 31 October 2012 (2012-10-31) the whole document	1-15
A	US 2012141685 A1 (GAAB MANUELA ET AL.) 07 June 2012 (2012-06-07) the whole document	1-15
A	US 2005004404 A1 (BASF AG ET AL.) 06 January 2005 (2005-01-06) the whole document	1-15
A	Andrew R.Millward et al. "Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature" *J. AM. CHEM. SOC.*, Vol. VOL.127, No. NO.51, 01 December 2005 (2005-12-01), ISSN: ISSN:1520-5126, pages:17998-17999	1-15

☐ 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 **13 January 2015**	Date of mailing of the international search report **26 January 2015**
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2014/064724

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