

surface of an inorganic matrix or of a ceramic membrane has been modified by covalently binding an organic functional group on said surface directly on the metal M<sup>1</sup>. In particular, the present invention aims to provide a method which is highly versatile, allowing a broad variety of modifications of surfaces of matrices or membranes.

The invention also aims to provide an organic functionalized matrix, i.e. a matrix of which a surface has been modified with organic functional groups, and in particular aims to provide a organic functionalized ceramic membrane that has adequate thermal and/or hydrothermal stability and that shows poor or substantially reduced leaching of attached groups. Another object of the invention is to provide an organic functionalized matrix, and in particular an organic functionalized ceramic membrane, which can be modified in a controlled manner and which has a high modification degree.

## SUMMARY

The present invention ~~describes~~provides a solution to at least some of the above-mentioned problems by providing a method for the modification of metal hydroxide and/or metal oxide surfaces of an inorganic matrix with an organometallic reagent for obtaining an organic functionalized matrix. The present invention ~~describes~~provides a method for preparing surface-modified matrices, i.e. matrices or membranes of which a surface has been modified or functionalized with an organic functional group. The present invention ~~describes~~provides a method for surface modification of a matrix involving the direct covalent binding of organic functional group(s) onto a surface of such matrix.

In an ~~example first aspect~~, the invention thereto ~~describes~~provides methods for the modification of metal hydroxide and/or oxide surfaces of an inorganic matrix with an organometallic reagent for obtaining an organic functionalized matrix, more particularly a functionalized matrix suitable for filtration processes. In a ~~first aspect~~particular embodiments, the invention ~~refers to~~provides methods for obtaining an organic functionalized matrix characterized by the direct covalent bond of one or more different organic functional moieties to its surface comprising the steps of:

- a) drying the inorganic matrix under vacuum,
- b) removing protons of the dried inorganic matrix by reacting said dried matrix with a reagent, whereby said reagent is preferably an alcohol,
- c) removing the excess of said reagent, preferably alcohol,

- a) reacting the dried matrix obtained in step c) in the presence of a dry solvent with an organometallic reagent, and
- b) optionally washing and further drying the obtained organic functionalized matrix.

In particular embodiments, the invention provides methods wherein the organometallic reagent is of the formula  $R^1-M^2$  or of formula  $R^1-M^2-X$  or of the formula  $R^1-M^2-R^{1'}$ , wherein  $R^1$  and  $R^{1'}$  are organic functional groups as defined herein and wherein  $R^1$  and  $R^{1'}$  are different or identical,  $M^2$  is Li or Mg, and X is a halogen. Preferably said organometallic reagent is selected from the group comprising organolithium reagents of general formula  $R^1-Li$  and organomagnesium reagents (Grignard reagents) of general formula  $R^1-Mg-X$  or of general formula  $R^1-M^2-R^{1'}$ , wherein  $R^1$  and  $R^{1'}$  are organic functional groups as defined herein ( $R^1$  and  $R^{1'}$  can be different or identical), and wherein X is selected from the group consisting of Cl, Br, I, and any mixtures thereof.

In another preferred embodiment, the invention provides a method wherein said metal ( $M^1$ ) is a Group IVb transition metal or mixtures thereof. More preferably, a method is provided wherein said transition metal is titanium or zirconium, and any mixtures thereof.

In particular embodiments, the invention provides methods wherein the alcohol of step b) is of formula  $R^2-OH$  wherein  $R^2$  is an alkyl, and particularly a linear  $C_1-C_8$  alkyl, more preferably a  $C_1-C_4$  and most particularly a  $C_1$  alkyl. In particular exampleembodiments  $R^2$  is a linear  $C_4$  alkyl.

In particular embodiments, the invention provides methods wherein step b) is performed for at least several hours, preferably more than 3 hours and most preferably 48 hours at the reflux temperature of said alcohol.

In particular embodiments, methods are provided wherein the matrix obtained in step b) is dried under vacuum prior to step d).

In particular exampleembodiments, the invention provides methods wherein step d) is carried out at room temperature preferably for between 1 and 6 days.

In particular embodiments, the invention provides methods wherein step d) is carried out at a temperature which is lower than the boiling point of said dry solvent.

In particular embodiments, methods are provided wherein said steps b) to d) are carried out under inert atmosphere, preferably under argon atmosphere.

In accordance with particular embodiments the methods according to the invention are repeated one or more times.

The present invention thus relates to methods for the modification of a surface of an inorganic matrix involving the direct covalent binding of a  $R^1$  or  $R^{1'}$  moiety or group, herein also referred to as an organic group or as an organic functional group, to a surface of said matrix, by the application of organometallic chemistry, i.e. by using organometallic reagents such as e.g. Grignard reagents and organolithium reagents.

A beneficial feature of the present methods compared to other modification methods is the versatility of these methods towards possible organic functional groups. The present methods allow a broad variety of different types of matrix/membrane modifications: the present methods permit to prepare organic-inorganic (hybrid) materials with a broad range of possible organic functional groups on a surface thereof, e.g. hydrophobic groups, selective adsorption sites, anchoring groups etc., by means of organometallic reactions on an inorganic matrix that has been pretreated, and in particular that has been deprotonated. Organic functional groups that can be directly covalently bound to a matrix according to the present invention are very diverse and a large amount of organometallic reagents are available and/or can be synthesized following general synthesis approaches for organometallic reagents, known in the art.

The present methods therefore also advantageously allow a specific modification/functionalisation of inorganic matrixes in function of their desired uses. For instance, specifically functionalized matrices are highly desired for certain applications, e.g. for use in specific filtration processes in which surface functionalisation is relevant in order to increase fluxes, improve separation/selectivity, prevent or stimulate adsorption of certain molecules, create anchoring sites for catalysts/ enzymes and other molecules or organisms. In an example, if highly hydrophobic matrices are to be obtained, the present method for instance involves the binding of group(s) with relatively long carbon chains possibly in combination with methyl functional groups to prevent steric hindrance. In another example, the bonding of moieties comprising fluorocarbons is also a suitable way to obtain hydrophobic matrices.

The present methods can also be applied for the preparation of multiple modified inorganic matrices that have various different moieties of a same class or of different classes directly covalently bound to their surface. This can be achieved by a repeated functionalisation and/or by the addition of different organometallic reagents in the reaction mixture during step d) of the present method. Therefore, even more versatile matrices towards  $R^1$  groups and more strongly functionalized matrices can be obtained.

In particular example embodiments, the present methods allow pore size engineering: i.e. defining pore size of modified inorganic matrices. Moreover, both pore size engineering and

functionalisation/modification can be done simultaneously. By changing the length of the carbon chains in the  $R^1$  or  $R^{1'}$  moieties and/or by multiple and/or repeated modifications with  $R^1$  or  $R^{1'}$  moieties and/or by the nature of the  $R^1$  or  $R^{1'}$  moieties, the pore diameter of the membranes can be decreased.

In another ~~example~~ aspect, the invention ~~describes~~ provides organic functionalized matrixes obtainable or obtained by carrying out methods according to the invention.

In a second aspect, the present invention refers to an organic functionalized matrix obtainable by carrying out a method as defined above, wherein the direct covalent binding of the organic functional groups to the surface of the substrate is obtainable via an M-C bond not including an oxygen bridge, wherein M is a metal.

The invention provides organic functionalized matrices, wherein said matrix is an inorganic filtration membrane comprising a support made of inorganic material coated with at least one separating membrane layer comprising particles of transition metal hydroxides and/or transition metal oxides at the surface having an average pore size of 1 to 10 nm.

In a third aspect~~particular embodiments~~, the present invention ~~refers to~~ provides inorganic filtration membranes obtainable with a method according to the invention comprising a support made of inorganic material coated with at least one separating membrane layer comprising particles of transition metal hydroxides and/or oxides at the surface on which are directly covalently grafted an organic functional group obtainable with the method according to the invention, wherein the direct covalent binding of the organic functional groups to the surface transition metal hydroxides and/or transition metal oxides is obtained via an M-C bond not including an oxygen bridge, wherein M is a metal. In a preferred embodiment, an inorganic filtration membrane is provided, wherein the organic functional group ( $R^1$  or  $R^{1'}$ ) directly covalently bound to the surface is chosen from the group comprising alkyl, (per)fluoroalkyl, aryl, (per)fluoroaryl and any combinations thereof.

An organic functionalized matrix is ~~described~~ provided having one or more  $R^1$  or  $R^{1'}$  moieties, as defined herein, that are directly bound covalently to a metal group on a surface of said matrix thereby providing more stable organic-inorganic interfaces. This type of direct covalent binding of  $R^1$  or  $R^{1'}$  moieties to a surface of a matrix greatly improves stability of the obtained matrix when applied in a broad range of preparation, application and cleaning conditions. The improved stability of surface-modified matrices disclosed herein originates from a strong direct covalent bonding, represented with formula  $M^1-C$ , with  $M^1$  referring to the metal as defined

7a

herein, and preferably a transition metal of group IVb, comprised within said matrix, and C referring to a carbon atom in a group R<sup>1</sup> or R<sup>1'</sup> as defined herein, in which said R<sup>1</sup> or R<sup>1'</sup> group is directly, covalently bond via a carbon atom to the metal centre on the matrices' surface. Therefore, rehydrolysis and bond breaking of the bound R<sup>1</sup> or R<sup>1'</sup> moieties is greatly prevented and no leaching of the R<sup>1</sup> or R<sup>1'</sup> organic functional group occurs. Compared to other modified ceramic membranes, surface-modified ceramic membranes according to the present invention are more versatile towards the type and amount of different functional groups R<sup>1</sup> or R<sup>1'</sup> and will be able to

resist more critical conditions even at sub-monolayer coverage, such as e.g. more solvent streams, including water and alcohols, e.g. for longer times, and for instance also at elevated temperatures, allowing applications of the present matrices in a wide variety of conditions and feed compositions.

As compared to other techniques commonly known in the art, the methods according to the present invention ~~describe~~<sup>provide</sup> in the direct covalent binding of the organic functional groups to the surface of the matrix. The resulting M<sup>1</sup>-C bond does not include an oxygen bridge, which is contrary to the commonly known methods. This greatly improves the stability of the obtained matrix. Compared to grafting with for instance organominerals such as organosilane, which typically forms a M-O-Si-R covalent bond, the stability of the M-R covalent bond with the method according to the present invention provides a bond which is not hydrolysable and provides therefore in a highly stable and highly efficient membrane.

Surface-modified matrices obtained or obtainable by carrying out a method according to the invention have a high functionalization degree and can be functionalized in a targeted adjustable manner. Also, surface-modified membranes obtained or obtainable by carrying out a method as disclosed herein show an improved stability, i.e. show lower amounts of organic functional groups that will leach from the membranes when used under certain temperature or solvent conditions. The herein disclosed surface-modified membranes are therefore suitable for use in various technical, biotechnological, pharmaceutical, food and medical fields.

~~In a fourth aspect example~~<sup>view thereof, in yet another aspect, the present invention refers</sup> is directed to the use of an organic functionalized matrix according to the invention or of an inorganic filtration membrane according to invention. In particular embodiments, the invention relates to the use of an organic functionalized matrix according to the invention or of an inorganic filtration membrane according to invention in filtration and/or adsorption and/or separation processes.

In particular ~~example~~<sup>embodiments</sup>, the invention relates to the use of an organic functionalized matrix according to the invention or of an inorganic filtration membrane according to invention as support, e.g. for catalyst systems, for enzyme systems, for molecules or organisms, etc.

Other benefits, advantages and uses of the invention will become apparent upon reading and understanding the below given specification.