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(54) Title: PREPARATION OF CAPROLACTONE, CAPROLACTAM, 2,5-TETRAHYDROFURAN-DIMETHANOL, 1,6-HEXANEDIOL OR 1,2,6-HEXANETRIOL FROM 5-HYDROXYMETHYL-2-FURFURALDEHYDE

(57) Abstract: The present invention relates to a method for preparing caprolactone, comprising converting 5-hydroxymethyl-2-furfuraldehyde by hydrogenation into at least one intermediate compound selected from the group of 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol and 1,2,6-hexanetriol, and preparing caprolactone from said intermediate compound. Further, the invention relates to a method for preparing 1,2,6-hexanetriol comprising preparing 5-hydroxymethyl-2-furfuraldehyde from a renewable source, converting 5-hydroxymethyl-2-furfuraldehyde into 2,5-tetrahydrofuran-dimethanol and converting 2,5-tetrahydrofuran-dimethanol into 1,2,6-hexanetriol. Further, the invention relates to a method for preparing 1,6-hexanediol from 1,2,6-hexanetriol, wherein 1,2,6-hexanetriol is subjected to a ring closure reaction, thereby forming (tetrahydro-2H-pyran-2-yl)methanol, and the (tetrahydro-2H-pyran-2-yl)methanol is hydrogenated, thereby forming 1,6-hexane diol.



Preparation of caprolactone, caprolactam, 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol from 5-hydroxymethyl-2-furfuraldehyde

The invention relates to a method for preparing epsilon-caprolactone (hereinafter referred to as: caprolactone). The invention further relates to a method for preparing epsilon-caprolactam (hereinafter referred to as: caprolactam) from caprolactone.

5 Caprolactone is amongst others a useful product to prepare caprolactam from. It is also used as a raw material for the preparation of polyesters and resins. Caprolactam is a much used monomer for the preparation of polyamide.

Industrially, caprolactone and caprolactam are generally obtained from starting compounds that are obtained from mineral oil, such as benzene or toluene. In
10 view of a growing desire to prepare materials using more sustainable technology it would be desirable to provide a method wherein caprolactone or caprolactam is prepared from a compound that can be obtained from a biologically renewable source. Furthermore, it would be desirable to provide a method that has a smaller ecological footprint than conventional chemical processes making use of bulk chemicals from
15 petrochemical origin, in particular a method that requires less energy and/or has a lower carbon dioxide emission than said conventional processes.

It has been proposed to prepare caprolactam from a biochemically obtained intermediate, making use of genetically modified micro-organisms that are capable of converting a biologically renewable starting material (such as a sugar) into the
20 intermediate. *E.g.* WO 2005/068643 describes the preparation of 6-aminocaproic acid by a genetically modified micro-organism. The 6-aminocaproic acid can thereafter be converted into caprolactam. Unfortunately, the titres of the obtained 6-aminocaproic acid and/or caprolactam in the Examples are low: in the order of ppm's, indicating that the reaction proceeds relatively slow, which is undesirable when operating at an
25 industrial scale.

WO2005/123669 relates to the production of caprolactam by heating a salt of L-lysine in a solvent comprising an alcohol. The lysine may be obtained from biomass. The current production process of lysine from biomass, produces lysine at a

price which is higher than the market price of caprolactam. In addition, the process uses expensive sulfonated hydroxylamine. Thereby this process is not really interesting for industrial use, in practice. Moreover, the production of sulfonated hydroxylamine is thought to be relatively energy-intensive.

5 It would be desirable to provide a method for preparing caprolactone or caprolactam from a starting compound that can be obtained from a biologically renewable source which does not require the use of a micro-organism. In particular, known processes making use of a microorganism have a low conversion rate. Further, the final concentration of the product of interest (caprolactam, caprolactone or a
10 precursor for any of these) is generally low. Therefore, it is contemplated a process based on a microorganism is not likely to produce caprolactone and caprolactam at competitive prices (at least not in the near future, because of the generally slow fermentation process and the low product concentration obtained in such a process.

 Also, the isolation of the product of interest from the culture medium
15 comprising the micro-organism used for the preparation of the product is generally relatively complex. Further, upscaling to a high-capacity plant and/or reducing reaction times may be an issue. Furthermore, there may be legal issues or consumer acceptance issues with respect to making use of genetically modified organisms that could frustrate implementation of the microbiological product of an intermediate for
20 caprolactone or caprolactam on an industrial scale. Finally, fermentative processes may produce considerable waste streams (cell mass, growth medium) which will evoke considerable effort with respect to its disposal in an acceptable manner.

 It is an object of the present invention to provide a method for preparing caprolactone or for preparing caprolactam from caprolactone from a starting
25 compound that can serve as an alternative to known methods. In particular it is an object to provide a method for preparing caprolactone or for preparing caprolactam wherein one or more of the above mentioned issues with prior art technology are overcome or at least alleviated.

 One or more further objects that may be addressed by the present
30 invention will be apparent from the description herein below.

 The inventors have found that it is possible to prepare caprolactone, caprolactam, 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol

from 5-hydroxymethyl-2-furfuraldehyde (HMF), which can be prepared from a renewable resource.

Accordingly, the present invention relates to a method for preparing caprolactone, comprising converting 5-hydroxymethyl-2-furfuraldehyde by
5 hydrogenation into at least one intermediate compound selected from the group of 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol and 1,2,6-hexanetriol, and preparing caprolactone from said intermediate compound.

Further, the present invention relates to a method for preparing 1,2,6-hexanetriol, comprising preparing 5-hydroxymethyl-2-furfuraldehyde from a
10 renewable source, converting 5-hydroxymethyl-2-furfuraldehyde into 2,5-tetrahydrofuran-dimethanol and converting 2,5-tetrahydrofuran-dimethanol into 1,2,6-hexanetriol.

Further, the present invention relates to a for preparing 1,6-hexanediol, comprising preparing 5-hydroxymethyl-2-furfuraldehyde from a renewable source,
15 converting 5-hydroxymethyl-2-furfuraldehyde into 2,5-tetrahydrofuran-dimethanol and converting 2,5-tetrahydrofuran-dimethanol into 1,6-hexanediol.

Further, the invention relates to a method for preparing 1,6-hexanediol from 1,2,6-hexanetriol, wherein 1,2,6-hexanetriol is subjected to a ring closure reaction, thereby forming (tetrahydro-2*H*-pyran-2-yl)methanol also abbreviated as 2-
20 THPM), and the (tetrahydro-2*H*-pyran-2-yl)methanol is hydrogenated, thereby forming 1,6-hexane diol.

Further, the present invention relates to a method for preparing caprolactam comprising reacting caprolactone prepared in a method according to the invention.

25 The invention is in particular advantageous in that the methods of the invention can readily be carried out on a large scale, because the HMF can be prepared from an abundant renewable source, such as fructose, and because the methods can be carried out without using a micro-organism to prepare the HMF from the renewable source and without using a micro-organism to prepare caprolactone,
30 caprolactam, 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol from HMF.

The term "or" as used herein is defined as "and/or" unless specified otherwise.

The term “a” or “an” as used herein is defined as “at least one” unless specified otherwise.

When referring to a noun (*e.g.* a compound, an additive, etc.) in the singular, the plural is meant to be included. Thus, when referring to a specific moiety,
5 *e.g.* "compound", this means "at least one" of that moiety, *e.g.* "at least one compound", unless specified otherwise.

Percentages (%) are weight percentages based on total weight, unless specified otherwise.

The term ‘renewable source’ is used herein in particular for materials that
10 can be naturally replenished from living organisms. Fossil materials that have been transformed by geological processes, such as coal, oil or the like, are not renewable sources. More in particular, renewable sources include biomass which may be obtained from living material (*e.g.* plant matter, or components isolated there from such as lignocellulose, cellulose, starch, or glucose). A preferred source of biomass is
15 agricultural waste (agro waste), which is formed by parts of agricultural crops that are not used for animal or human consumption. Normally it would be composted, largely to CO₂.

The HMF may in principle be obtained in any way, in particular from any renewable source. Preferably, the HMF has been prepared from a carbohydrate. The
20 carbohydrate may in particular be selected from the group of fructose, glucose, sucrose, starch, cellulose and lignocellulose, including mixtures of any two or more of these, *e.g.* a mixture comprising glucose and fructose.

HMF can be prepared from fructose by an acid-catalysed dehydration reaction. This may be accomplished in a manner known *per se*, for instance in
25 aqueous/organic mixtures, catalysed by sulphuric acid as described by Dumesic and co-workers (*Nature* 2007, 447, 982-985) or in DMSO catalysed by LaCl₃ (Ishida and co-workers, *Chemistry Letters* 2000, 22-23). Another method is described in Joseph B. Binder, and Ronald T. Raines, *J. Am. Chem. Soc.*, **2009**, 131 (5), 1979-1985. Further, several reviews exist that describe the various processes, such as: Dumesic and co-
30 workers, *Angewandte Chemie International Edition*, 2007 46 7164-7183 and B. F. M. Kusters, *Starch*, 1990, 8, 314-321. The contents of these publications regarding the reaction conditions of preparing HMF are incorporated by reference.

If a carbohydrate polymer is used, this may first be depolymerised to provide monosaccharide units (*e.g.* glucose or fructose). This may be accomplished in a manner known *per se*.

If glucose is used to prepare HMF, the glucose may first be converted into fructose, *e.g.* in a manner known *per se*. For instance, in a suitable process a product comprising glucose, such as corn syrup or another starch product, is first liquefied using an alpha-amylase, then the liquified product is enzymatically converted into glucose using a glucoamylase, and thereafter the product treated with glucoamylase is treated with glucose isomerase to give a mixture of fructose and glucose. This mixture can be separated, *e.g.* by simulated moving bed (SMB) to give what is called High Fructose Cornstarch Syrup (HFCS90), in case the starting product is corn syrup. This typically contains about 90 wt. % of fructose, based on dry weight. Of course, other syrups providing fructose may be used. HFCS90 is a preferred raw material for the production of HMF.

The conversion of HMF into 1,6-hexanediol may be done in any way.

In an advantageous embodiment, HMF is hydrogenated, thereby forming 2,5-tetrahydrofuran-dimethanol (THFDM), and thereafter THFDM is hydrogenated, thereby forming 1,6-hexanediol.

The 1,6-hexanediol can thereafter be converted into caprolactone.

This dual hydrogenation pathway is advantageous for a number of reasons. First of all the hydrogenolysis of the ether linkage needs high temperatures and high pressures. Under these conditions, undesired decarbonylation of HMF can be quite rapid. Therefore, it is preferred to first hydrogenate the aldehyde function to an alcohol and concomitantly the two double bonds of the furan under mild conditions to the THF-dimethanol before embarking on the hydrogenolysis of the two ether bonds that take place at higher temperatures. An advantage is that the first hydrogenation step can be performed with (cheap) Raney nickel. Potential impurities that are present in the HMF can be absorbed on this cheap catalyst before the process stream reaches the second, generally more expensive catalyst, thereby prolonging life-time of the second catalyst.

The hydrogenation of HMF to THFDM may be accomplished in a manner known *per se*, for instance as described by Schiavo *et al.* in J. Bulletin de la Soci   Chimique de France (1991), p 704-11.

The hydrogenation of HMF to THFDM is usually carried out in the presence of hydrogen gas and a hydrogenation catalyst. A suitable hydrogenation catalyst may in particular be selected from the group of nickel catalysts, such as Raney nickel, or nickel nanoparticles, either in solution or on a carrier material, palladium, (e.g. on active coal or on another carrier material or in the form of nanoparticles), ruthenium (on carbon, in the form of nanoparticles or on another carrier material), rhodium (on carbon, in the form of nanoparticles or on another carrier material), platinum (on carbon, in the form of nanoparticles or on another carrier material), iron (on carbon, in the form of nanoparticles or on an other carrier material), gold (on carbon, in the form of nanoparticles or on other carrier material) or copper chromite. Nickel catalysts are preferred. Especially preferred is the use of Raney nickel or the use of nickel nanoparticles. It is also possible to use mixtures of catalysts. The ratio (W/W) of catalyst to HMF preferably is in the range of 1:1 to 1:1000 more preferred ratios are in the range of 1:2 to 1:100

As used herein, the term 'nanoparticles' means particles of a solid or semi-solid material having a weight average diameter, as determinable by scanning electron microscopy (SEM) or transmission electron microscopy (TEM) in the range of 1-1000 nm, in particular in the range of 5-500 nm.

The hydrogenation may conveniently be carried out in a flow reactor, such as a continuous stirred tank reactor (CSTR) or a tube reactor. The hydrogenation is preferably carried out in a solvent. Protic solvents or water are preferred solvents. Ethanol and propanol are particularly preferred solvents.

The molar ratio hydrogen gas to HMF is in general at least stoichiometric. Preferably an excess hydrogen gas is used. In particular, the molar ratio may be in the range of 10 to 2000. The hydrogen pressure preferably is between 1 and 12 MPa (10 and 120 bar) a more preferred range is 5-10 MPa (50-100 bar).

The temperature during the hydrogenation of HMF is usually chosen in the range of 50-250 °C, in particular in the range of 60-150 °C; preferred is a temperature in the range of 70-110 °C.

The hydrogenation of THFDM to 1,6-hexanediol may be accomplished in a manner known *per se*, for instance as described in US 3,070,633, of which the contents are incorporated herein by reference.

In particular, the hydrogenation of THFDM may be carried out with hydrogen gas in the presence of a hydrogenation catalyst. A suitable hydrogenation catalyst may in particular be selected from the group of copper based catalysts, more in particular copper catalysts in which at least one further metal-element is present.

5 The metal-element needs not be in a metallic state. Examples of copper catalyst including at least one further metal element are copper chromite and copper zinc.

Other catalysts that can be used include on rhodium on a solid support, such as rhodium on silica. The rhodium catalyst may be doped with one or more other elements. A preferred dopant is rhenium.

10 The hydrogenation of THFDM may be carried out in a conventional hydrogenation reactor, in particular in a CSTR or a tube reactor.

The hydrogenation of THFDM may be carried out in an inert solvent (*e.g.* an inert alcohol, such as methanol, ethanol or 1-propanol, a cycloalkane, such as cyclohexane, or in dimethoxymethane) or in the absence of an inert solvent.

15 The molar ratio hydrogen gas to THFDM is in general at least stoichiometric. Preferably an excess hydrogen gas is used. In particular, the molar ratio may be in the range of 10 to 2000.

The temperature during the hydrogenation of THFDM is usually chosen in the range of 80-350 °C, in particular in the range of 120-330 °C. A preferred
20 temperature used may depend on the type of catalyst used. A preferred range for use with copper chromite is from 250-320 °C. A preferred range for use with a Rh/Re catalyst is 120-250 °C.

The hydrogen pressure during the hydrogenation of THFDM is usually chosen in the range of 5-20 MPa (50-200 bar); a preferred hydrogen pressure is
25 between 8-12 MPa (80-120 bar).

The substrate to catalyst ratio(w/w) is usually chosen between 1:1 and 500:1; a preferred range is from 4:1 to 50:1.

In a preferred method, the first and the second hydrogenation step are directly coupled in the sense that the hydrogenation of HMF and the hydrogenation of
30 the product of the HMF hydrogenation reaction are carried out in the same reactor, or in the sense that the product of the HMF hydrogenation reaction is continuously fed from a first reactor into a second reactor or from a first reaction zone inside a reactor (wherein the first hydrogenation reaction is carried out) into a second reaction

zone inside that reactor (wherein the second hydrogenation step is carried out). In particular, the product of the HMF hydrogenation reaction may be directly fed from the first reactor or first reaction zone into the second reactor or first reaction zone. As used herein, 'directly fed' in particular means fed without intermediate storage of the product, without intermediate chemical reaction steps, and without intermediate purification steps. The second hydrogenation preferably takes place at higher temperature than the first hydrogenation. Accordingly, if desired, the feed may be heated when being transferred from the first to the second hydrogenation step. The product then can be converted into caprolactone.

5 In an embodiment of the above second hydrogenation, THFDM is hydrogenated to 1,2,6-hexanetriol or 1,6-hexanediol, which then can be converted into caprolactone, if desired.

Various catalysts can be used for this hydrogenation such as those based on palladium, nickel, rhodium, ruthenium, molybdenum, copper and chromium or mixtures thereof. Rhodium is a preferred metal. These catalysts may be deposited on a carrier material, such as silica, alumina or titanium oxide. In particular good results have been achieved with silica and titanium oxide. More in particular, good results were observed with G-6 3 silica from Fuji. The catalysts may also be doped with other elements such as rhenium, molybdenum and tungsten. A preferred catalyst is a rhodium-rhenium catalyst, in particular a rhodium-rhenium catalyst on silica. Much preferred is a Rh/Re catalyst on G-6 3 silica from Fuji.

20 The molar ratio of hydrogenation catalyst (such as rhodium) to dopant (such as rhenium) may be chosen within wide ranges, in particular in the range of 100: 1 to 1:100. Preferably said ratio is in the range of 10:1 to 1:10; even more preferred is a ratio between 1:2 and 2:1.

25 Preferred temperatures are between 80-160 °C, more preferred between 100-140 °C.

Pressures may in particular be between 4 and 14 MPa, (between 40 and 140 bar) preferably between 6 and 10 MPa (between 60 and 100 bar).

30 The hydrogenation is preferably carried out in a solvent. Protic solvents or water are preferred solvents. Ethanol and propanol are more preferred solvents.

The 1,2,6-hexanetriol may be further hydrogenated to 1,6-hexanediol using a catalyst based on palladium, nickel, rhodium, ruthenium, copper and chromium or

mixtures thereof. These catalysts may be deposited on a carrier material, for example silica. They may also be doped with one or more other elements, such as rhenium. A preferred catalyst is based on copper chromite.

5 The hydrogenation of 1,2,6-hexanetriol may be carried out in a conventional hydrogenation reactor, in particular in a CSTR or a flow reactor.

The hydrogenation of 1,2,6-hexanetriol may be carried out in an inert solvent (*e.g.* an inert alcohol, such as methanol, ethanol or 1-propanol, a cycloalkane, such as cyclohexane, or in dimethoxymethane) or in the absence of a solvent.

10 The molar ratio hydrogen gas to 1,2,6-hexanetriol is in general at least stoichiometric. Preferably an excess hydrogen gas is used. In particular, the molar ratio may be in the range of 10 to 2000.

The temperature during the hydrogenation of 1,2,6-hexanetriol is usually chosen in the range of 150-350 °C. The temperature used may depend on the type of catalyst used. A preferred range for use with copper chromite is from 250-320 °C.

15 The hydrogen pressure during the hydrogenation of 1,2,6-hexanetriol is usually chosen in the range of 5-20 MPa (50-200 bar), preferably in the range of 8-12 MPa (80-120 bar).

The substrate to catalyst ratio (w/w) usually is chosen in the range of 1:1 to 500:1; a preferred range is from 4:1 to 50:1.

20 In yet a further embodiment, HMF is directly converted into 1,6-hexanediol or 1,2,6-hexanetriol.

For instance, HMF may be hydrogenated with hydrogen in the presence of copper chromite as a hydrogenation catalyst, thereby producing 1,6 hexanediol or 1,2,6-hexanetriol. Suitable reaction conditions may *e.g.* be based on US 3,083,236 on
25 which the contents are incorporated by reference, in particular Example IV(a).

To suppress decarbonylation which may happen during hydrogenation, any of the hydrogenations in accordance with the invention may be carried out in the presence of CO (or a precursor for CO). A precursor for CO is a compound that under the hydrogenation conditions reacts to form CO. Precursors can in particular be
30 selected from formic acid and formic acid esters. The amount of CO (or precursor for CO) relatively to hydrogen may in particular be in the range of 0.01-1, preferably in the range of 0.01 and 0.1 (mole to mole).

As indicated above, the invention also relates to a method for preparing 1,6-hexanediol from 1,2,6-hexanetriol, wherein 1,2,6-hexanetriol is subjected to a ring closure reaction, thereby forming (tetrahydro-2*H*-pyran-2-yl)methanol, and the (tetrahydro-2*H*-pyran-2-yl)methanol is hydrogenated, thereby forming 1,6-hexane diol. An advantage of such method is its high selectivity. The 1,2,6-hexanetriol may in principle be obtained in any way. Advantageously, it is made from THFDM, as described elsewhere in the present disclosure. Thereby, this method of preparing 1,6-hexanediol makes it possible to prepare 1,6-hexanediol from THFDM with a high overall selectivity.

The ring-closure reaction is conveniently catalysed by an acidic catalyst. This may be a solid acid catalyst, such as an acidic zeolite or a silica alumina catalyst or sulphated zirconia or an acidic ion exchange material, in particular an acidic ion exchange resin.

A suitable zeolite may in particular be selected from the group of ZSM-5 zeolites (silica) and beta-zeolites.

The acidic ion exchange material may in particular be selected from the group of materials having sulfonate groups as functional groups. In particular good results have been achieved with Smopex101®, sulfonated styrene divinylbenzene copolymers, such as Amberlyst™, or a sulfonated fluoropolymer, such as Nafion (e.g. Nafion SAC-13). In a further embodiment, the acidic catalyst is a soluble acid, such as an aromatic or aliphatic carboxylic acid, such as acetic acid, trifluoroacetic acid or benzoic acid or an aliphatic or an aromatic sulfonic acid, such as methanesulfonic acid, or trifluoromethanesulfonic acid or para-toluenesulfonic acid or it may be an aliphatic or an aromatic phosphonic acid such as benzene phosphonic acid. It may also be a mineral acid, such as sulfuric acid or phosphoric acid. In practice strong acids such as trifluoromethanesulfonic acid are preferred.

The ring-closure reaction can be carried out without a solvent; however use of a solvent is preferred, as it leads to higher selectivities. In practice any solvent that is acid stable at the reaction temperature and in which the substrate is soluble may be used. Sulfolane is a preferred solvent.

The reaction is conveniently carried out at elevated temperatures, in particular at a temperature of at least 50 °C. In one embodiment of the invention the

reaction takes place using gaseous reagents and a solid acid catalyst, preferably at a temperature of 200°C or more. In another embodiment, the reaction takes place in the liquid phase, preferably at a temperature between 50 and 200 °C, more preferably at a temperature between 100 and 150 °C.

5 The hydrogenation of (tetrahydro-2H-pyran-2-yl)methanol to form 1,6-hexanediol may in principle be based on the hydrogenation conditions for hydrogenating THFDM, as described elsewhere in the present disclosure. In particular, good selectivity has been achieved with a rhodium-rhenium on silica catalyst. The molar ratio rhodium to rhenium may in particular be in the range of
10 100: 1 to 1:100; preferably between 10:1 and 1:10; more preferred is a ratio between 1:2 and 2:1.

 In a particularly preferred method according to the invention 1,2,6-hexanetriol is formed by hydrogenating 5-tetrahydrofuran-dimethanol, which may have been obtained from a renewable source, converting 1,2,6-hexanetriol, thus
15 obtained, into (tetra-hydro-2H-pyran-2yl) methanol (2-THPM), and converting 2-THPM, thus obtained into 1,6-hexanediol. This method offers in particular a good selectivity and yield towards 1,2,6-hexanetriol and 1,6-hexanediol (an overall selectivity of at least 95 % at 57 % THFDM conversion has been found feasible, or an overall selectivity of at least 86 % at complete THFDM conversion).

20 If desired, the method may be carried out at an incomplete conversion of 1,2,6-hexanetriol to 1,6-hexanediol. Then, the 1,6-hexanediol can be recovered from the product obtained from the reaction, which product then comprises both 1,2,6-hexanetriol and 1,6-hexanediol, and the 1,2,6-hexanetriol is then recycled to the reaction, if desired. The recovery of 1,6-hexanediol can be accomplished in a manner
25 known *per se*.

 The formation of 1,2,6-hexanetriol and the formation of 1,6-hexanediol is generally catalysed by a hydrogenation catalyst. The formation of 2-THPM is generally catalysed by a ring closure catalyst (usually an acidic catalyst). The reaction steps may be carried out as described elsewhere herein. A preferred hydrogenation
30 catalyst is a rhodium-rhenium catalyst, in particular a rhodium-rhenium catalyst on silica. A preferred ring closure catalyst is an acidic ion exchange material, in particular an acidic ion exchange resin or other ion exchange material having

sulfonate groups as functional groups. Particularly preferred is a sulfonated fluoropolymer, such as Nafion.

In particular, good results have been achieved with such a method, wherein the 1,2,6-hexanetriol, the (2-tetra-hydro-2H-pyran-2yl) methanol, and the
5 1,6-hexanediol are formed in a one-pot process. It is contemplated that in particular the combined presence of a hydrogenation catalyst and a dehydration catalyst is advantageous for obtaining 1,6-hexanediol in a good yield, in particular a yield of 86 % or more.

It is also possible to immobilise the hydrogenation catalyst onto the surface
10 of an acidic solid acid catalyst. A preferred catalyst is Rh/Re on Nafion SAC-13.

The 1,6-hexanediol thus obtained may thereafter be used for the preparation of caprolactone in accordance with the invention, or used for another purpose.

The preparation of caprolactone from 1,6-hexanediol may be accomplished
15 in any way. The preparation of caprolactone from 1,6-hexanediol is a so-called lactonisation of a diol. Such processes have been known in the art for over 40 years. For this conversion it is possible to use at least one catalyst selected from the group of homogeneous metal catalysts and heterogeneous metal catalysts. Many heterogeneous catalysts are suitable for this process. Catalysts may be based on
20 ruthenium, osmium, rhodium, iridium, palladium, platinum, copper, cobalt, vanadium nickel or iron. These metals may be entered as catalysts in an oxidised form or in a reduced form. Usually the heterogeneous catalyst will be supported on a carrier material. Examples of suitable carrier materials include silica, alumina, active carbon, and barium sulphate.

For instance, caprolactone may be prepared in a method comprising
25 mixing (vaporised) 1,6-hexanediol with hydrogen, contacting the mixture with a catalyst, such as copper oxide, and recovering the formed caprolactone. Such conversion may be based on a method described in US 3,317,563 (published in 1967), of which the contents, in particular the conditions specified in claims 1-6 and in the
30 examples, are incorporated by reference.

Further, caprolactone may be prepared from 1,6-hexanediol, using silver carbonate, *e.g.* on celite. Suitable conditions may be based on Tetrahedron (1975), 31(2), 171-6, of which the contents are incorporated by reference.

Further, caprolactone may be prepared by treating 1,6-hexanediol with oxygen or a gas comprising oxygen (*e.g.* in air) in the presence of a transition metal catalyst; suitable examples are gold, nickel, ruthenium, rhodium, iridium, platinum or a palladium catalyst. The catalysts may be in the form of a homogeneous catalyst,
5 containing ligands or they may be a heterogeneous catalyst on a carrier, such as silica, alumina or carbon, or they may be in the form of nanoparticles. Suitable conditions may for instance be based on JP 55 024 107, JP 61 048 509 or JP 2010208968A, of which the contents are incorporated by reference.

Further, caprolactone may be prepared by oxidative lactonisation of 1,6-
10 hexanediol with sodium bromite, *e.g.* based on a method described in Chemistry Letters (1983), (7), 1097-100 or in JP 59 025 383, of which the contents are incorporated by reference.

Further, caprolactone may be prepared from 1,6-hexanediol in the presence of Preyssler's anion as a catalyst using hydrogen peroxide as oxidant.
15 Suitable conditions may be based on Bamoharram *et al.*, Journal of Molecular Catalysis A: Chemical 252 (2006) 90-95 of which the contents are incorporated by reference.

In an advantageous embodiment, the conversion of 1,6-hexanediol into caprolactone is carried out in the presence of a homogeneous transition metal catalyst
20 that is active as a redox catalyst. In general, any catalyst that is active as transfer hydrogenation catalyst or as racemisation catalyst is suitable. Many review articles and book chapters have been written about these catalysts, such as G. Zassinovich, G. Mestroni, S. Gladiali, *Chemical Reviews*, **1992**, 92, 1051-1069. D. Klomp, U. Hanefeld, J. A. Peters in *Handbook of Homogeneous Hydrogenation*, J. G. de Vries, C. J. Elsevier, eds., Wiley-VCH, Weinheim, 2007, Vol 1, p585-630. Yangsoo Ahn, Soo-
25 Byung Ko, Mahn-Joo Kim, Jaiwook Park, *Coordination Chemistry Reviews* 252 (2008) 647-658. These catalysts can be based on ruthenium, osmium, rhodium, iridium, palladium, platinum, copper, cobalt, vanadium nickel or iron, in particular on ruthenium, iridium, cobalt and nickel. In general, the homogeneous catalyst for
30 converting the 1,6-hexanediol into caprolactone will be in the form of a complex. In particular they may comprise one or more ligands selected from the group of phosphorus based ligands, alkoxides, amines, arenes, CO, substituted cyclopentadienes, unsubstituted cyclopentadienes; cyclometallatable CN ligands (*i.e.*

ligands that bind via an anionic carbon atom and a neutral or anionic nitrogen atom that are linked together), CP ligands (*i.e.* ligands that bind via an anionic carbon atom and a neutral or anionic phosphorus atom that are linked together), CNN ligands (*i.e.* ligands that bind via an anionic carbon atom and two nitrogen groups that are linked together), CPP ligands (*i.e.* ligands that bind via one anionic carbon atom and two phosphorus atoms selected from the group of neutral phosphorus atoms and anionic phosphorus atoms that are linked together) and other cyclometallatable ligands.

Phosphorus based ligands include monodentate phosphines, bidentate phosphines, phosphites, phosphonites, phosphinites and phosphoramidites.

Amines include amines having more than one amine per molecule, *e.g.* diamines. Examples of amines that can be used as ligands include pyridine, bipyridine and 1,10-phenanthroline.

Cyclometallatable CN ligands include benzylamine, *N*-methyl-benzylamine *N,N*-dimethyl-benzylamine.

CP ligands include tris-ortho-tolyl-phosphine. CNN ligands include 1,3-dimethylaminomethylbenzene.

CPP ligands include 1,3-bis-(diphenylphosphinomethyl)benzene.

A ligand can further be selected from solvent molecules having ligand properties, such as tetrahydrofuran (THF) or acetonitrile. The complex of ligand(s) and metal may also have one or more anions selected from the group of halides, carboxylates and non-coordinating anions, such as BF_4^- or PF_6^- .

Good results have been achieved with iridium complexes, such as $[\text{Cp}^*\text{IrCl}_2]_2$ or with ruthenium complexes, in particular with complexes of the type $\text{Ru}(\text{phosphine})_n\text{X}_m$ where $n = 1, 2, 3$ or 4 and $m = 1, 2$ or 3 , or mixtures thereof. Also particularly suitable are complexes made *in situ* by the addition of monodentate or bidentate phosphorus ligands to $[\text{Ru}(\text{arene})\text{Cl}_2]_2$ in which arene is benzene, cymene or trimethylbenzene.

The molar ratio of substrate to catalyst may in particular be between 1 and 1 000 000. Preferred is a molar ratio in the range of 100-200 000.

Often these catalysts need the presence of a catalytic amount of a base, for good catalytic activity. The base can be a mineral base, for instance a mineral base selected from the group of KOH, NaOH, KHCO_3 , K_2CO_3 , Na_2CO_3 , Cs_2CO_3 and

NaHCO₃, or it can be an organic base, for instance triethylamine, tributylamine or DABCO (1,4 diazabicyclo[2.2.2]octane).

The molar ratio of the catalyst to the base may vary considerably and may also be dependent on the catalyst employed. In general said molar ratio will be in the range of from 1:1 to 1: 100 000; preferably from 1:5 to 1:100.

The lactonisation may be carried out as a dehydrogenation in which hydrogen is formed as side product. This hydrogen is optionally used for the hydrogenation of HMF to 1,6-hexanediol or of THFDM to 1,6-hexanediol or of 1,2,6-hexanetriol to 1,6-hexanediol. It is also possible to carry out the lactonisation in the presence of a hydrogen acceptor or an oxidant. Suitable hydrogen acceptors include ketones, such as acetone, or methyl isobutylketone (MIBK) or alkenes such as isobutene. The resulting alcohols may be used as such or may be dehydrogenated to regenerate the ketone and an equivalent of hydrogen. The lactonisation may also be carried out in the presence of an oxidant such as oxygen or hydrogen peroxide.

The lactonisation may be carried out without a solvent or in the presence of a suitable solvent that is inert to the reaction conditions, such as a hydrocarbon or a halogenated hydrocarbon. It is also possible to use a ketone which participates in the reaction as a hydrogen acceptor as solvent. In a preferred method wherein use is made of a homogenous cyclisation catalyst, the conversion of the 1,6-hexanediol into caprolactone is carried out in the presence of a phase transfer catalyst. The phase transfer catalyst (PTC) is preferably selected from the group of quaternary ammonium salts, in particular from the group of tetraalkylammonium salts, and polyalkylene glycols, in particular polyethylene glycols. The alkyl group will generally comprise 1 to 20 carbon atoms. The counter ion may be a halide, such as chloride or bromide, or HSO₄⁻ or acetate or tosylate. In general the choice of the anion is not critical. Examples of suitable PTC's are tetrabutylammonium bromide or benzyltrimethylammonium chloride or tetra-octylammonium hydrogen sulfate. The amount of PTC with respect to the amount of substrate is between 0.01-50 mol%; more preferred is between 1-25 mol%. The temperature of the reaction may vary between 50-200 °C; more preferred between 80-150 °C.

Caprolactam can be prepared from caprolactone in a manner known *per se*. In a preferred method of the invention caprolactam is prepared in a method comprising reacting caprolactone with ammonia. Suitable processes are *e.g.* described

in US 3,000,880, US 3,025,306 and US 3,064,008, of which the contents are incorporated by reference, in particular the contents dealing with the reaction conditions for preparing caprolactam from caprolactone.

5 The invention will now be illustrated by the following examples.

Example 1 Direct hydrogenation of HMF to 1,6-hexanediol

10 In a stirred autoclave of 100 ml 0.1 g of copper chromite and 0.06 g of Pd on carbon (10 %) was added to a solution of 0.5 g of HMF in 25 ml of methanol. The lid of the autoclave was closed, stirring was started at 1000 rpm and after three vacuum/nitrogen cycles the autoclave was pressurised at 3 MPa H₂ and the temperature was raised to 80 °C. After 1.5h the hydrogen pressure was raised to 15 MPa and the temperature to 270 °C. The autoclave was kept stirred under these
15 conditions for a further 14.5 h. After cooling to ambient temperature the pressure was released and the contents of the autoclave were subjected to GC analysis, which showed the presence of 4.2% of 1,6-hexanediol and 2.3% of 1,2,6-hexanetriol.

Examples 2-15 Hydrogenation of HMF to THFDM.

20 In a stirred autoclave of 100 ml 0.05 g of 5 Mol% Ru/C (Aldrich) was added to a solution of 0.5 g of HMF in 30 ml of methanol. The lid of the autoclave was closed, stirring was started at 1000 rpm and after three vacuum/nitrogen cycles the autoclave was pressurised at 5 MPa H₂ and the temperature was raised to 75 °C. After 1.5 h the
25 hydrogen pressure was raised to 9 MPa and the temperature to 200 °C. The autoclave was kept stirred under these conditions for a further 14 h. After cooling to ambient temperature the pressure was released and the contents of the autoclave were subjected to GC analysis, which showed the presence of 30% of THFDM.

30 In the same manner several other catalysts were tested in this hydrogenation and the results are collected in Table 1

Table 1 Hydrogenation of HMF to 2,5-THF-dimethanol ^a

Example	Catalyst	%-2,5-THF-dimethanol
2	Ru/C (ALD) 5%	30
3	Ru/C (JM) 5%	46
4	Ru/C (JM) 0.5%	12
5	Pd/C 10%	38
6	G-69B (Sud)	55
7	Ra-Ni	79
8	CuCr (ALD)	9
9	CuCr (AC)	11
10	CuCr-Pd/C	62

Suppliers between brackets: ALD=Aldrich; JM=Johnson Matthey; Sud=sudchemie; AC=Across

^a In all cases 100% conversion of the starting material was observed.

5

From these results it is clear that Raney nickel (Ra-Ni) is a very good catalyst for this conversion.

10 Examples 11-15 (summarised in Table 2) show the effect of the temperature on the hydrogenation of HMF with Raney nickel at 9 MPa in methanol.

Table 2: Hydrogenation of HMF with Ra-Ni at different temperatures. ^a

Examples	Temperature	Yield of 2,5-THF-dimethanol
11	250	50
12	200	79
13	150	88
14	100	99
15	75	91

^a In all cases 100% conversion of the starting material was observed.

From these examples it is clear that 100 °C is an optimal temperature for the hydrogenation of HMF to THFDM with Ra-Ni, and that Ra-Ni is a suitable catalyst.

5 Example 16-22 Hydrogenation of THFDM to 1,6-hexanediol.

In a stirred autoclave of 100 ml 0.1g of copper chromite was added to a solution of 0.5 g of THFDM in 30 ml of *n*-propanol. The lid of the autoclave was closed, stirring was started at 1000 rpm and after three vacuum/nitrogen cycles the autoclave
10 was pressurised at 10 MPa H₂ and the temperature was raised to 260 °C. The autoclave was kept stirred under these conditions for a further 6 h. After cooling to ambient temperature the pressure was released and the contents of the autoclave were subjected to GC analysis, which shows the presence of 17.3 % of 1,6-hexanediol and 3.7% of 1,2,6-hexanetriol. Other catalysts were tested under similar conditions
15 (Table 3).

Table 3: Hydrogenation of THFDM

Example	Catalyst	Conversion	Yield 1,6-hexanediol	Yield 1,2,6-hexanetriol
16	CuCr	70%	17.3%	3.7%
17	CuZn (JM PR-A)	26%	1.8%	5.4%
18	CuZn (JM PR-B)	71%	2.1%	2.0%
19	CuZn (Sud T-2 130)	28%	2.2%	1.1%

In the Examples 20-22 the effect of temperature and duration on the
20 hydrogenation of THFDM with CuCr was investigated in experiments which were performed otherwise identical to Example 16.

Table 4: Hydrogenation of THFDM with CuCr

Example	Time	Temperature	1,6-hexanediol	1,2,6-hexanetriol
20	6h	260 °C	17%	4%
21	15h	260 °C	22%	1%
22	6h	320 °C	15%	0%

Preparation of Rh/Re catalyst for use in Examples 23-32

5 Silica was precalcined at 773K for 3h prior to impregnation unless otherwise mentioned. Two grams of silica were stirred with an aqueous solution of 176 mg of RhCl_3 during 2 hours. Thereafter the water was filtered off and the remaining solid dried at 383K for 13-14h. Next, the solid was impregnated with an aqueous solution of 113 mg of NH_4ReO_4 , after filtration and drying as before the final
10 step was calcination in air at 773K for 3h.

The catalyst was measured to have a Rh-content of 4 wt-% and a Re-content of 2 wt%.

It is also possible to apply the two solutions in a single impregnation step. The catalyst prepared in this fashion was tested in Example 24.

15 It is also possible to use carrier materials other than silica such as Alumina or Cerium oxide.

For comparison purposes catalysts were also prepared that were only impregnated with Rh (tested in Example 25) or with Re (tested in Example 26) according to the procedure described above. Results with all four types of catalysts
20 can be found in Table 5.

Example 23-32 preparation of 1,2,6-hexanetriol

In an autoclave of 60 ml, 25 mg of the Rh/Re catalyst prepared according to
25 the procedure above was added to a solution of 100 mg of THFDM in 29 ml of water. The autoclave was closed, stirring was started at 1000 rpm and after 3 vacuum nitrogen cycles the hydrogen pressure was set at 1 MPa and the temperature at 120 °C. After 1 h the hydrogen pressure was raised to 8 MPa. After 4h the autoclave was

allowed to cool to ambient temperature and the pressure was released. Analysis of the contents by GC showed a conversion of THFDM of 16.5%, a yield of 1,2,6-hexanetriol of 7.5% and a yield of 1,2,6-hexanetriol of 0.4%.

In the examples 23-32 different catalysts, catalyst mixtures and carrier materials were tested in the hydrogenation of THFDM. These reactions were performed in capped glass vials that contained a stir bar the septum of which had been pierced with a needle to equalise the pressure. Up to 6 of these vials were hydrogenated at the same time in the autoclave.

Table 5 Hydrogenation of THFDM to mainly 1,2,6-hexanetriol

Example	Catalyst	%-conv	%-yield 1,6	%-yield 1,2,6	%-sel 1,6	%-sel 1,2,6
23	Rh-Re/SiO ₂ ^a (2-step) ^d	16.5	0.4	7.5	2.2	45.7
24	Rh-Re/SiO ₂ ^a (1-step) ^e	15.3	0.0	6.8	0.0	44.2
25	Rh/SiO ₂	3.1	0.0	0.0	0.0	0.0
26	Re/SiO ₂	3.4	0.0	0.0	0.0	0.0
27	Rh-Re/CeO ₂ (2-step) ^d	9.5	0.0	2.0	0.0	21.0
28	Rh-Re/Al ₂ O ₃ (2-step) ^d	4.0	0.0	0.0	0.0	0.0
29	Rh/Al ₂ O ₃ + Re	10.5	0.0	4.4	0.0	42.4
30	Rh/Al ₂ O ₃	2.1	0.0	0.0	0.0	0.0
31	Rh-Re/SiO ₂ ^b (2-step) ^d	14.1	0.0	10.4	0.0	73.9
32	Rh-Re/SiO ₂ ^c (2-step) ^d	30.9	1.0	25.8	3.4	83.5
33	Rh 4 wt. % Re/Rh 0.5 (mol/mol)	11	0.0	10.3	0.0	94

^a Silica grade 9385 (Aldrich) ; ^b Silica G-6 5 mikron (Fuji Silysia) ; ^c Silica G-6 3 mikron (Fuji Silysia);

^d First impregnation with Rh, followed by impregnation with Re in a second step.

^e Simultaneous impregnation with Rh and Re in a single step

These experiments show it is possible to hydrogenate THFDM with high selectivity to 1,2,6-hexanetriol, when a combination of rhodium and rhenium is used.

Example 34 Hydrogenation of 1,2,6-hexanetriol to 1,6-hexanediol

In an autoclave of 100ml 0.1 g of CuCr(BASF) was added to a solution of 0.5 g of 1,2,6-hexanetriol in n-propanol. After three vacuum/nitrogen cycles stirring
 5 was started at 1000 rpm, the autoclave was pressurised with hydrogen to 10 MPa and the temperature is raised to 260 °C. After 6h the autoclave was allowed to come to ambient temperature and the pressure was released. GC of the contents showed a 40% yield of 1,6-hexanediol.

10 Example 35: Lactonisation of 1,6-hexanediol

A 50 ml three-necked flask flask was provided with a reflux condensor a nitrogen inlet and a magnetic stir bar. K₂CO₃ (0.2 mmol) was added, followed by 1 mmol of 1,6-hexanediol and 25 ml of acetone. The solution was subjected to 3
 15 vacuum/nitrogen cycles and 2 mol% of [Ir(Cp*)Cl]₂ (Cp* = pentamethyl-cyclopentadiene) was added. The mixture was kept under nitrogen and heated under reflux while stirring for 24h. After this period GC showed 44% conversion with a selectivity of 33% to caprolactone.

20 Example 36- 3: Lactonisation of 1,6-hexanediol

In examples 36-38 other catalysts were tested in the lactonisation of 1,6-hexanediol to caprolactone (Table 6).

Table 6: Lactonisation of 1,6-hexanediol

Example	Catalyst	Conversion	Selectivity to caprolactone
35	[Cp*IrCl ₂] ₂	44%	33 %
36	RuCl ₂ (PPh ₃) ₃	31%	81%
37	[p-cymenRuCl ₂] ₂ +dppp*	54%	87%
38	RuCl ₃ +dppp	3%	90%

* dppp=1,3-(Diphenylphosphino)propane

25

In Examples 39-45 three catalysts were tested in the same way as in Example 35, with the difference that different solvents were tested.

Table 7: Lactonisation of 1,6-hexanediol

Example	Catalyst	Solvent	Conversion	Selectivity to caprolactone
39	[Cp*IrCl ₂] ₂	acetone	44%	33%
40		MIBK	10%	57%
41	RuCl ₂ (PPh ₃) ₃	acetone	31%	81%
42		MIBK	64%	76%
43		CHCl ₃	3%	
44	[<i>p</i> -cymeneRuCl ₂] ₂ + dppp	acetone	54%	87%
45		MIBK	87%	90%

5 Examples 46 and 47: Lactonisation of 1,6-hexanediol

In these examples the lactonisation of 1,6-hexanediol was performed according to the method described in example 34 using MIBK as solvent and K₂CO₃ as base. In these two experiments 20 mol% of Bu₄NBr was additionally added. These results show that the addition of a phase transfer catalyst to these lactonisation reactions is beneficial. The results are displayed in Table 8.

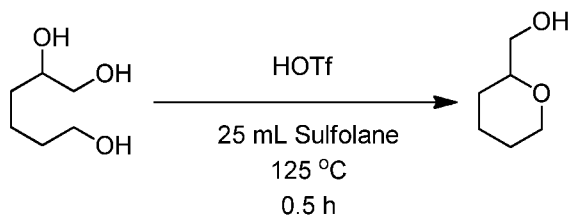
Table 8

Example	Catalyst	PTC	Conversion	Selectivity to caprolactone
46	RuCl ₂ (PPh ₃) ₃	Bu ₄ NBr (20 mol%)	95%	97%
47	[RuCl ₂ (<i>p</i> -cymene)] ₂ , dppp	Bu ₄ NBr (20 mol%)	99%	98%

15 Examples 48-49 preparation of 1,6-hexanediol from 1,2,6-hexanetriol

1,2,6-hexanetriol was converted into (tetrahydro-2*H*-pyran-2-yl)methanol:

23



The reaction was performed in a 100 mL three-neck round bottom flask. 1,2,6-hexanetriol (3.3543 g, 25.0 mmol) was dissolved in sulfolane (25 mL). Then, trifluoromethanesulfonic acid (13.3 μ L, 0.15 mmol,) were added. The reaction mixture was heated to 125 °C for 30 mins. GC shows full conversion with 100% selectivity to the desired product.

Next, 0.1 g of (tetrahydro-2*H*-pyran-2-yl)methanol (THPM) was put in an 8 ml vial and the vial was filled with water (2 g) as the solvent. The catalyst (10 mg, 10 %-wt to THPM) was added to the solution. The vial was then put in a stainless steel autoclave. The autoclave was sealed and five times pressurised with hydrogen gas and vented in order to remove air. First, the pressure and temperature were set to 1 MPa and 180 °C, respectively. After 1 h, the pressure was increased to 8 MPa and the reaction was stopped after 3.5 h.

The results are shown in Table 9.

Table 9

Example	Catalysts	%-conv	%-sel. to 1,6-hexanediol
48	Rh-Re/SiO ₂ JM ^a	16,6	100
49	Rh-Re/SiO ₂ Fujj ^{b,c}	8,3	100

^a 6,5%-wt Rh

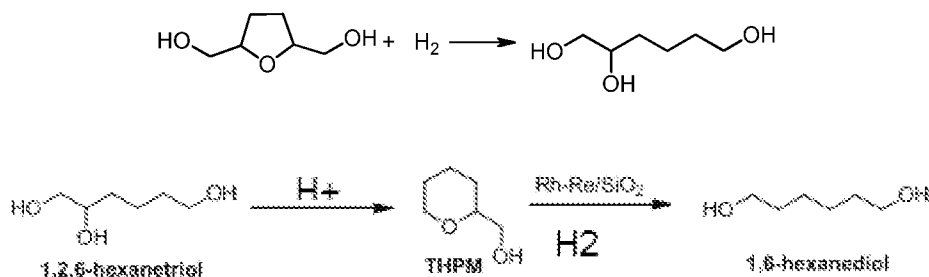
^b 4%-wt Rh

^c when the reaction was performed for 20 h (instead of 3.5 h): 8.6%-conv and 100%-selectivity to 1,6-hexanediol

Example 50-62: preparation of 1,6 hexanediol from THFDM (via 1,2,6-HT and 2-THPM)

1,6 hexanediol was prepared from THFDM using the following reactions in a single pot..

24



The reactions were carried out on 100 mg of 2,5-THF-dimethanol in 2 g of
 5 water in a single stirred autoclave (one-pot process), with Rh-Re (6.5 wt. % Rh; Re/Rh
 = 0.5) on SiO₂ from Johnson Matthey as hydrogenation catalyst (25 weight% w.r.t.
 the starting material) and various acidic catalysts (ring closure catalyst) in 15 weight
 % w.r.t. the starting material. The conditions were as follows: temperature = 120 °C.
 The pressure was 1 MPa for the first hour and thereafter 8 MPa for the remaining 19
 10 hours.

The results are shown in Table 10. The selectivity to the major side
 product, 1,5 hexanediol, is also shown.

Table 10:

Example	acidic catalyst	t ₂ (h)	%-conv	%-sel to 1,6 hexanediol	%-sel to 1,5 hexanediol	%-sel to 1,2,6 hexanetriol
50	Sulfonated carbon	20	65	26	4	70
51	Sulfonated carbon	4	22	9	1	90
52	Zeolite 1	20	82	39	9	52
53	Zeolite 1	4	37	15	0	81
54	Zeolite 2	20	92	61	12	27
55	Zeolite 2	4	38	18	0	77
56	Zeolite 3	20	87	47	7	46
57	Zeolite 3	4	29	9	0	88
58	Nafion [®] SAC-13	20	100	86	14	0
59	Nafion [®] SAC-13	4	57	21	0	74
60	Sulph-ZrO ₂	20	88	49	9	42
61	Amberlyst [™] -16	20	91	56	10	34
62	Smopex [®] -101	20	93	60	10	30

15

Zeolite 1 is ZAP-27 (Si/Al = 12.5) and Zeolite 2 is ZAP-55 (Si/Al = 21.1) (these are types of
 ZSM-5 silica see: I. Melián-Cabrera, C. Mentrut, J.A.Z. Pieterse, R.W. van den Brink, G. Mul,
 F. Kapteijn, A. Moulijn, Catalysis Communications 6 (2005) 301–305.); and Zeolite 3 is 814E

(a type of beta zeolite from Zeolyst International, $\text{SiO}_2/\text{Al}_2\text{O}_3$ Molar Ratio: 25). For the preparation of sulfonated carbon, see Example XX below

It is shown that 100 % conversion is obtained with sulfonated fluoropolymer (Nafion® SAC-13) as the acidic catalyst, within 20 hours, with 86 % selectivity towards 1,6 hexanediol. The results for other catalysts are also satisfactory in that the selectivity to desired products (1,6-hexanediol and 1,2,6 hexanetriol) is high (more than 85 %)

10 Example 63 Preparation of Sulfonated Carbon

20 g of D-glucose was heated up to 400 °C (5 °C/min) under a N_2 flow in a tubular oven for 15 h to produce brown-black solids. The obtained solids were weighed and then ground to powder. The produced powder was heated in concentrated H_2SO_4 (95-97% Merck) at 150 °C under N_2 for 15 h to introduce SO_3H groups into the aromatic carbon rings (30 ml H_2SO_4 per gram). After cooling to room temperature, the solids were filtered using 1000 cm^3 of distilled water. Subsequently, the black precipitates were washed repeatedly with hot distilled water ($T > 80$ °C) until no acidity was detected in the residual water. The material was placed in a petri dish and dried overnight in an oven at 90 °C. Composition: $\text{CH}_{0.55}\text{O}_{0.57}\text{S}_{0.013}$. Total acidity: 1,61 mmol/g. SO_3H -density: 0.61 mmol/g

Claims

1. Method for preparing caprolactone, comprising converting 5-hydroxymethyl-2-furfuraldehyde by hydrogenation into at least one intermediate compound selected from the group of 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol
5 and 1,2,6-hexanetriol, and preparing caprolactone from said intermediate compound.
2. Method according to claim 1, wherein the 5-hydroxymethyl-2-furfuraldehyde is obtained from a renewable source.
3. Method according to claim 1 or 2, wherein 5-hydroxymethyl-2-furfuraldehyde is hydrogenated, thereby forming 2,5-tetrahydrofuran-dimethanol,
10 and said 2,5-tetrahydrofuran-dimethanol is hydrogenated, thereby forming 1,6-hexanediol and/or 1,2,6-hexanetriol.
4. Method according to claim 3, wherein 5-hydroxymethyl-2-furfuraldehyde is hydrogenated in the presence of a Raney nickel hydrogenation catalyst or another nickel catalyst.
- 15 5. Method according to claim 1-3, wherein 2,5-tetrahydrofuran-dimethanol is hydrogenated in the presence of a copper chromite hydrogenation catalyst.
6. Method according to any of the claims 3-5, wherein 1,2,6-hexanetriol is formed by hydrogenating 2 5-tetrahydrofuran-dimethanol, 1,2,6-hexanetriol is converted into (2-tetra-hydro-2*H*-pyran-2yl)methanol,
20 (2-tetra-hydro-2*H*-pyran-2yl)methanol is converted into 1,6-hexanediol, and the caprolactone is prepared from the 1,6-hexanediol.
7. Method according to claim 6, wherein the 1,2,6-hexanetriol, the (2-tetra-hydro-2*H*-pyran-2yl) methanol, and the 1,6-hexanediol are formed in a one-pot process.
- 25 8. Method according to any of the preceding claims, wherein the conversion of 1,6-hexanediol into caprolactone is carried out in the presence of a homogenous cyclisation catalyst, a base and a phase transfer catalyst.
9. Method according to claim 8, wherein the cyclisation catalyst is selected from the group of ruthenium complexes, iridium complexes, cobalt complexes and

nickel complexes, the base is selected from the group of alkali metal carbonates, and the phase transfer catalyst is selected from the group of quaternary ammonium salts and polyalkylene glycols, in particular from the group of tetraalkylammonium salts.

10. Method according to any of the preceding claims, wherein 5-

5 hydroxymethyl-2-furfuraldehyde is prepared from a carbohydrate.

11. Method according to claim 10, wherein the carbohydrate is selected from the group of fructose, glucose, starch, cellulose and lignocellulose, including mixtures thereof.

12. Method for preparing caprolactam comprising reacting caprolactone
10 prepared in a method according to any of the preceding claims with ammonia.

13. Method for preparing 1,2,6-hexanetriol comprising preparing 5-hydroxymethyl-2-furfuraldehyde from a renewable source, converting 5-hydroxymethyl-2-furfuraldehyde into 2,5-tetrahydrofuran-dimethanol and converting 2,5-tetrahydrofuran-dimethanol into 1,2,6-hexanetriol.

15 14. Method according to claim 13, wherein the renewable source is selected from the group of carbohydrates, in particular from the group of fructose, glucose, starch, cellulose and lignocellulose, including mixtures thereof.

15. Method according to claim 12 or 13, wherein the converting of 2,5-tetrahydrofuran-dimethanol into 1,2,6-hexanetriol is catalysed by a rhodium rhenium
20 catalyst.

16. Method for preparing 1,6-hexanediol comprising converting 1,2,6-hexanetriol obtained in a method according to any of the claims 13-15 into 1,6-hexanediol.

17. Method for preparing 1,6-hexanediol from 1,2,6-hexanetriol, optionally
25 according to claim 16, wherein 1,2,6-hexanetriol is subjected to a ring closure reaction, thereby forming (tetrahydro-2H-pyran-2-yl)methanol, and the (tetrahydro-2H-pyran-2-yl)methanol is hydrogenated, thereby forming 1,6-hexane diol.

18. Method according to claim 17, comprising hydrogenating 1,2,6-hexanetriol, thereby forming 1,6-hexanediol.

30 19. Method for preparing 1,6-hexanediol from 2,5-tetrahydrofuran-dimethanol, optionally according to claim 16, 17 or 18, comprising the steps of hydrogenating 2,5-tetrahydrofuran-dimethanol to 1,2,6-hexanetriol, ring-closing 1,2,6-hexanetriol to (tetrahydro-2H-pyran-2-yl)methanol and hydrogenating (tetrahydro-

2H-pyran-2-yl)methanol to 1,6-hexanediol, in which said steps are performed in a one-pot process.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2011/050200

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D201/08 C07D309/30 C07D313/04
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)
C07D

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 practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	OKA, SHINZABURO: "Studies on lactone formation in vapor phase. II. Synthesis of .epsilon.-caprolactone", BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, vol. 35, no. 4, April 1962 (1962-04), pages 562-566, XP002603786, the whole document	1-11
Y	US 4 400 468 A (FABER MARCEL [US]) 23 August 1983 (1983-08-23) the whole document	1-11
X	US 3 070 633 A (TORLEIF UTNE ET AL) 25 December 1962 (1962-12-25) cited in the application	13-15
Y	column 1, line 44 - line 46 column 1, line 54 - line 55	1-11
	-/--	



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 document but published on or after the international filing date
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"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

14 April 2011

Date of mailing of the international search report

21/04/2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2011/050200

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 083 236 A (TORLEIF UTNE ET AL) 26 March 1963 (1963-03-26) cited in the application the whole document -----	1-11
Y	INOUE, YOSHIHISA; DEGUCHI, SHOKICHIRO; HAKUSHI, TADAO: "A convenient one-step preparation of oxacyclanes by dehydration of diols over alumina", BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, vol. 53, no. 10, 1980, pages 3031-3032, XP002603787, the whole document -----	16-19
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Y	CHEN, KAIYOU; KOSO, SHUICHI; KUBOTA, TAKESHI; NAKAGAWA, YOSHINAO; TOMISHIGE, KEIICHI: "Chemoselective Hydrogenolysis of Tetrahydropyran-2-methanol to 1,6-Hexanediol over Rhenium-Modified Carbon-Supported Rhodium Catalysts", CHEMCATCHER, vol. 2, no. 5, 15 March 2010 (2010-03-15), pages 547-555, XP002603789, the whole document -----	16-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2011/050200

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4400468	A	23-08-1983	NONE	
US 3070633	A	25-12-1962	NONE	
US 3083236	A	26-03-1963	NONE	