

A HETEROGENEOUS CATALYST

The invention is directed to a heterogeneous catalyst comprising carrier particles having a carrier surface and to which carrier surface a metal-complex, and a halogen salt are immobilized. The heterogeneous catalyst is especially suited for preparing a cyclic carbonate starting from an epoxide and carbon dioxide.

The use of carbon dioxide as a cheap and readily available C1 source in fine and bulk chemical production is attracting significant interest. One of such chemical production routes is the synthesis of cyclic carbonates from ring-strained epoxides and CO₂. Cyclic carbonate products are used as electrolytes in Li-ion batteries. Further they may be used as monomers for polycarbonate synthesis and non-isocyanate polyurethanes or as synthetic intermediates.

Various high pressure processes are known such as described in EP2431363. This publication describes a process performed at 20 bar in the presence of a tetra(n-butyl) phosphonium bromide catalyst.

There is a desire to perform this reaction at more ambient pressure conditions. A suited catalyst for this reaction at lower pressures comprises a Lewis acid-base catalyst and a halogen salt as a source for a halide anion (X⁻). RAFIK RAJJAK SHAIKH ET AL: "Catalytic Strategies for the Cycloaddition of Pure Diluted, and Waste CO₂ to Epoxides under Ambient Conditions", ACS CATALYSIS, part B, no. 1, 5 January 2018 (2018-01-05), pages 419-450, XP055671558 describes various of such catalyst for the cyclic carbonate synthesis starting from an epoxide and carbon dioxide. In this article metal-organic complexes are described as the Lewis acids which perform well as a catalyst in the presence of a halogen salt and especially tetra-n-butylammonium bromide (TBAB). Examples mentioned in this article are aminotrisphenolate metal complexes. Possible metals mentioned are aluminium, gallium, indium, iron, cobalt, nickel, zinc, titanium and/or bismuth.

Further the oxo-dimer of a substituted salen aluminium complex is described as a possible Lewis acid.

US2021/0355094 describes a catalyst comprising an ethylenediamino
5 bridged tetra(phenolate) rare earth-zinc heterobimetallic compound as the Lewis acid. The reaction of an epoxide and carbon dioxide is performed in the presence of this compound and tetra-n-butylammonium bromide (TBAB).

Gallium-organic complexes such as the gallium aminotrisphenolate
10 compounds which catalyse the cyclic carbonate synthesis starting from an epoxide and carbon dioxide in the presence of tetrabutylammonium iodide (TBAI) or tetrabutylammonium bromide (TBAB) are described in ChemCatChem 2021, 13, 4099–4110.

15 Many of the reported catalyst systems have been tested for this reaction in a homogenous reaction environment. For a commercial application it is advantageous to perform the reaction in the presence of a heterogeneous catalyst. This for example simplifies the separation of the catalyst and the formed cyclic carbonate.

20 WO2009/109765 describes a process to prepare cyclic carbonate compounds from carbon dioxide and an epoxide compound using a heterogeneous catalyst system comprising an oxo-dimer of a substituted salen aluminium complex. This catalyst system requires a halogen ammonium salt
25 such as tetra-n-butylammonium bromide (TBAB) to be present in order to be catalytically active. Systems involving such dissolved ammonium salt are however not advantageous because of issues with this compound in downstream processing units. This is apparently solved in this patent by immobilizing the salen aluminium complex on a silica carrier via a
30 diethylammonium(propyl)ethyl group substituent on the phenyl group of the complex. The presence of this diethylammonium(propyl)ethyl group not only anchors the complex to the silica carrier but also functions as the ammonium salt. Tetra-n-butylammonium bromide (TBAB) is however still required to be

added in order to activate the catalyst. A disadvantage is that it is found that tetra-n-butylammonium bromide leaches from the supported catalyst system.

5 The object of the present invention is to provide a supported catalyst system suited for the cyclic carbonate synthesis starting from an epoxide and carbon dioxide which does not leach a halogen salt such as tetra-n-butylammonium bromide.

10 This problem is solved by the following heterogeneous catalyst. Heterogeneous catalyst comprising carrier particles having a carrier surface, to which carrier surface a metal-complex and a halogen salt is immobilized and wherein the metal-complex and the halogen salt are each individually immobilized to the carrier surface.

15 Applicants have found that heterogeneous catalyst according to this invention can be advantageously used as a catalyst or as part of a catalyst in a chemical process in the presence of an organic halogen compound and in the absence of a non-immobilised halogen ammonium salt. The presence of this halogen compound enhances the activity of the catalyst and enhances the
20 activity when the catalyst is reused in for example subsequent batch or semi-batch operations to prepare the cyclic carbonate. This allows one to use this catalyst in chemical processes which are up to now catalysed by metal complexes and in the presence of a non-immobilised halogen ammonium salt. By using this catalyst in the presence of an organic halogen compound one
25 does not require the presence of the unwanted non-immobilised halogen ammonium salt. It is especially found that the heterogeneous catalyst of this invention can be used in a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide without leaching of a halogen ammonium salt.

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Furthermore the fact that the metal-complex and the halogen salt are each individually immobilized enables one to influence the relative presence of the halogen salt with respect to the metal complex in the catalyst.

Preferably an amine is also individually immobilized to the carrier surface next to the halogen salt and the metal complex. It is found that the heterogeneous catalyst more effectively binds carbon dioxide when an amine is also immobilised. This allows one to directly contact carbon dioxide containing gasses, such as flue gasses or cement kiln flue gasses, with the catalyst. The amine is preferably a tertiary amine and may be presented by the general formula $R^1R^2R^3N$ wherein R^1 is an anchoring group for covalently binding the tertiary amine to the carrier surface. R^2 and R^3 may be the same or different organic group and preferably the same or different alkyl group having from 1 to 20 carbon atoms, preferably 1-6 carbon atoms. R^2 and R^3 can also be part of a ring structure forming a 5- or 6 membered ring. R^2 or R^3 may also be an aminoalkyl group. Examples of compounds where R^2 and R^3 are part of a ring structure are morpholine, piperidine and pyrrolidine structured compounds. More preferably, R^2 and R^3 are preferably the same alkyl group for example the same methyl or ethyl group. R^1 may be an alkyl(trialkoxysilane anchoring group, wherein the alkyl group preferably has 2 to 6 carbon atoms and the alkoxy group has preferably 1 to 3 carbon atoms. R^1 may be an alkyltrichlorosilane, propyl(alkyl)dichlorosilane and a propyl(dialkyl)chlorosilane anchoring group wherein the alkyl group may have between 2 and 6 carbon atoms. Examples of these groups are propyl(trimethoxy)silane, propyl(triethoxy)silane, propyl(methyl)dichlorosilane and a propyl(dimethyl)chlorosilane and propyltrichlorosilane. R^1 may also be a styryl(trialkyl)silane, propylbis(methylallyl)silane, propyl, tris(methylallyl)silane, propylphosphoric acid, propyl(dialkyl)phosphonate, and alkyl-1,1 bisphosphonic acid wherein the alkyl group may have between 1 and 6 carbon atoms.

The halogen salt is preferably an ammonium or phosphonium halogen salt. The choice of the halogen will also decide the choice of any other halogen compound used as part of the catalyst system as they are preferably the same. This halogen is also referred to as the catalyst system halogen. Preferred halogen salts are iodide salts and bromide salts. The iodide salt which is

immobilised is preferably a phosphonium iodide salt and more preferably a quaternary ammonium iodide salt. The bromide salt which is immobilised is preferably a phosphonium bromide salt and more preferably a quaternary ammonium bromide salt. The quaternary ammonium iodide salt and the quaternary ammonium bromide salt may have the general formula $R^4R^5R^6R^7NX$, wherein X is a bromide or an iodide anion, R^4 is an anchoring group and R^5 , R^6 and R^7 may be the same or different alkyl or aryl groups preferably having between 1 and 20 carbon atoms. R^5 and R^6 can also be part of a ring structure forming a 5- or 6 membered ring. Examples of compounds where R^5 and R^6 are part of a ring structure are morpholine, piperidine and pyrrolidine structured compounds. Preferred groups R^5 , R^6 and R^7 are alkyl groups having between 1 and 20 carbon atoms, more preferably between 3 and 12 carbon atoms, such as for example propyl, n-butyl, iso-butyl, tert.-butyl, n-pentyl, neo-pentyl and iso-pentyl.

Anchoring group R^4 may be as described for anchoring group R^1 .

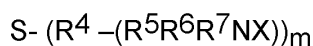
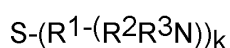
The metal- complex, alkylated amine and the halogen salt may be supported to the carrier surface by steric trapping, electrostatic binding and/or covalent binding. Preferably immobilization is performed by means of a covalent binding where an anchoring group is used.

For covalent binding, the solid support needs to contain or be derivatized to contain reactive functionalities which can serve for covalently linking an anchoring compound to the surface thereof. Examples of suitable reactive functionalities are titanol (Ti-OH), silanol and aluminol (Al-OH). Materials having such functionalities are for example silicon dioxide supports containing reactive silanol groups, alumina supports containing reactive aluminol groups, amorphous silica-alumina supports having both silanol and aluminol groups and sol-gel materials. Other possible carrier particles may be polyacrylamide supports, polystyrene supports and polyethylene glycol supports.

Preferred carrier particle is a titanium dioxide, silica, alumina and/or silica alumina particle. The silanol groups as present on the surface of the silica or silica-alumina particle and/or the aluminol groups as present on the surface of the alumina or silica-alumina particle or the titanol as present on the surface of the titanium dioxide particle are preferably covalently connected.

The catalyst particle may be relatively large when used as part of a packed bed in a reactor. In such a bed inert particles may be present. Preferably the heterogeneous catalyst is present as a suspension in a liquid reaction mixture. The support will then be present as a powder having dimensions which are small enough to create a high active catalytic surface per weight of the support and large enough to be easily separated from the cyclic carbonate in or external of the reactor. Preferably the support powder particles have for at least 90 wt% of the total particles a particle size of above 10 μm and below 2000 μm . The particle size is measured by a Malvern® Mastersizer® 2000.

The metal-complex, the halogen salt and the optional tertiary amine may suitably be individually immobilized to the carrier surface of the heterogeneous catalyst as presented below:



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wherein S is the carrier surface,

wherein the tertiary amine is $\text{R}^1\text{R}^2\text{R}^3\text{N}$ and wherein R^1 is an anchoring group which covalently binds the tertiary amine to the carrier surface S and R^2 and R^3 are the same or different alkyl group having from 1 to 20 carbon atoms or wherein R^2 and R^3 are part of a ring structure forming a 5- or 6 membered ring or R^2 or R^3 are amino alkyl groups,

30

wherein the quaternary ammonium halogen salt is $R^4R^5R^6R^7NX$,
wherein X is a bromide or an iodide anion, R^4 is an anchoring group which
covalently binds the quaternary ammonium halogen salt to the carrier surface S
and R^5 , R^6 and R^7 are the same or different alkyl groups having between 1
5 and 20 carbon atoms,

wherein R^8 is an anchoring group which covalently binds the metal
complex to the carrier surface S and

wherein k:m:n is the molar ratio of the amine, the halogen salt and the
metal-complex as individually immobilized to the carrier surface S.

10 The molar ratio of halogen salt and metal-complex is suitably 1:1 and
higher. Expressed for the above formula this would be that m is equal or
greater than n. When no amine is immobilized k will be equal to zero.

15 When the metal complex is an aluminium complex as for example
described in more detail below it is preferred that the molar ratio of k:m is
between 3:1 and 8:1. The molar ratio of n:k is preferably between 1:3 and 1:10
and more preferably between 1:3 and 1:5.

20 When the metal complex is a gallium complex as described in more detail
the molar ratio of k:m is preferably below 1:4 wherein k may be equal to zero.

When the carrier surface has silanol groups as present on the surface S
of the silica or silica-alumina particle and/or aluminol groups as present on the
25 surface S of the alumina or silica-alumina particle it is preferred that R^1 , R^4 and
 R^8 are the same or different alkyl(trialkoxysilane anchoring group and/or an
alkyltrichlorosilane anchoring group.

30 The metal as part of the metal-complex may be any one or more chosen
from the group of aluminium, gallium, indium, iron, cobalt, nickel, zinc, titanium
and/or bismuth. Also rare earth metal complexes may be used, such as Y, Sm,

Nd, and La polydentate N-methylethylenediamine-bridged tris(phenolato) ligands as described in ACS Sustainable Chem. Eng. 2020, 8, 13185–13194.

US2021/0355094 describes a catalyst comprising an ethylenediamino
5 bridged tetra(phenolate) rare earth-zinc heterobimetallic compound as the Lewis acid. The reaction of an epoxide and carbon dioxide is performed in the presence of this compound and tetra-n-butylammonium bromide (TBAB).

The metal-complex may be any catalytically active complex which is
10 activated by a halogen ammonium salt, preferably tetra-n-butylammonium bromide (TBAB). More preferably any metal-complex which is known to catalyse reactions involving carbon dioxide. Preferably the metal complex is an aminotrisphenolate metal complex. Examples are aminotrisphenolate
15 aluminium complexes as described in J. Am. Chem. Soc. 2013, 135, 1228-1231, Chem. Eur. J. 2014, 20, 2264-2275 and in Chem. Sus. Chem. 2017, 10, 1274-1282.

Possible aminotrisphenolate iron complexes are described in Inorg.
Chem. 2012, 51, 20, 10639–10649.

A preferred metal-complex is an aminotrisphenolate gallium complexes as
for example described in ChemCatChem 2021, 13, 4099-4110. It has been
found that good catalytic activity is achieved when tertiary amines are
individually immobilized and also when no tertiary amine is individually
25 immobilized. Preferably the molar ratio of individually immobilised halogen salt and individually immobilised metal-complex is suitably 1:1 and more preferably higher than 3:1 for this type of catalyst.

Possible vanadium complexes which are active in this reaction in the
30 presence of tert.-butyl iodide are described in ChemCatChem 2012, 4, 1190 – 1196.

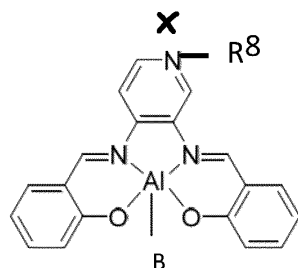
Another preferred metal complex is a salen-metal complex or its oxo-dimer and more preferably a salen-aluminium complex or its oxo-dimer and most preferably a salen-aluminium complex. For this type of catalyst, it is preferred that an amine is individually immobilized next to the halogen salt and the metal complex. The salen aluminium complex and/or its oxo-dimer may be the complexes described in the afore mentioned WO2009/109765. The salen aluminium complexes are preferably immobilized using an anchoring group. This anchoring group may be substituted to one of the phenyl groups which is typically part of these salen aluminium complexes as disclosed by WO2009/109765 or to the bridging group which connects the two nitrogen atoms of the salen aluminium complex. Preferably the anchoring group comprises a quaternary ammonium nitrogen which is paired with a halogen, preferably the catalyst system halogen. An example of such an anchoring group is diethylammonium(propyl)ethyl group as described in the earlier referred to WO2009/109765. This is advantageous because the quaternary ammonium nitrogen ion paired with the catalyst system halogen will then function as the co-catalyst of the heterogeneous catalyst of this invention.

A problem with the catalyst as described in WO2009/109765 is that the supported salen aluminium ligand is difficult to prepare requiring at least 9 synthesis steps. Some of these steps have a low yield resulting in an overall yield of less than 10% and large amounts of solvents are used in the synthesis process. Applicants have now found a complex which can be prepared in a much simpler method in a higher yield. This preferred salen aluminium complex and/or its oxo-dimer is an optionally substituted salen aluminium complex or its oxo-dimer having a pyridinium bridging group. The quaternary nitrogen ion of the pyridinium bridging group acts as a co-catalyst of the catalyst system and as a means to connect to an anchoring group R^8 for immobilization to the carrier surface.

The pyridinium bridging group may be a 2-pyridinium bridging group and preferably a 3-pyridinium bridging group allowing attachment of an anchoring group. The optionally substituted salen aluminium ligand having a salen

aluminium ligand having a 3-pyridinium bridging group may be presented by the following general formula:

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wherein B is a halogen, alkoxy or alkyl group,

and wherein the phenyl groups of the salen aluminium ligand are

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optionally substituted, where R^8 is an anchoring group and X is a halogen anion. The phenyl groups may be substituted at their 3-position. The alkoxy group B may be a methoxy, ethoxy and/or isopropoxy group. The alkyl group B may have 1-5 carbon atoms, such as for example methyl or ethyl. B may also be chloride, bromide or iodide. The choice of B may depend on the availability of the starting aluminium compound when synthesizing the complex. For this reason B is preferably chloride.

20

The anion X is suitably the catalyst system halogen which may be an iodide anion or a bromide anion.

25

The phenyl groups in the above formula's may be substituted with halogen, optionally substituted C1-20 alkyl, optionally substituted C5-20 aryl, optionally substituted C3-20 heterocyclyl, ether, ammonium and nitro groups. Examples are described in EP2146977. Preferably the phenyl groups are substituted with a butyl group and more preferably with a tert.-butyl group.

30

Anchoring group R^8 may be as described above for R^1 and R^4 .

The heterogeneous catalyst may comprise one of the following complexes illustrating different anchor groups R and different groups B:

5 [Al(3,4-Py-Salphen(N-Propyl(trimethoxy)silane))(Cl)]Br,
 Al(3,4-Py-Salphen(N-Propyl(triethoxy)silane))(Cl)]Br ,
 [Al(3,4-Py-Salphen(N-Propyl(triethoxy)silane))(OEt)]Br ,
 [Al(3,4-Py-Salphen(N-Propyl(triethoxy)silane))(Cl)]I,
 [Al(3,4-Py-Salphen(N-Propyl(diethoxyphosphonate)(Cl)]Br ,
 [Al(3,4-Py-Salphen(N-Propyl(phosphoric acid)(Cl)]Br ,
10 [Al(3,4-Py-Salphen(N-Butyl(diethyl phosphonate)(OEt)]Br , and
 [Al(3,4-Py-Salphen(N-Pentyl(phosphoric acid)(Cl)]Br,
 [Al(3,4-Py-Salphen(N-Propyl(trimethoxy)silane))(Et)]Br,
 [Al(3,4-Py-Salphen(N-Propyl(trimethoxy)silane))(OEt)]Br.

15 wherein for the above complexes optionally a substituent group is present at the 3-position of the phenyl groups of the salphen structure as described above. Further Et is ethyl and OEt is ethoxy in the above descriptions.

20 The heterogeneous catalyst comprising the immobilized optionally substituted salen aluminium complex having a pyridinium bridging group can be prepared by the following process.

25 Process to prepare an optionally substituted salen aluminium complex starting from a corresponding optionally substituted salen nickel or zinc complex having a 3-pyridine bridging group, wherein the following steps are performed:

- 30 (a) demetallizing the corresponding substituted salen nickel or zinc complex to obtain a demetallized salen ligand,
 (b) contacting the demetallized salen ligand of step (a) with an aluminium compound to obtain the optionally substituted salen aluminium complex having a 3-pyridine bridge, and

(c) subjecting the optionally substituted salen aluminium complex having a 3-pyridine bridge to an alkylation with an anchoring precursor compound to obtain the corresponding alkylated optionally substituted salen aluminium complex having a pyridinium bridging group and an anchoring group R8 attached to the quaternary nitrogen ion of the pyridinium bridging group, and
5 (d) immobilizing the alkylated optionally substituted salen aluminium complex obtained in step (c) on a carrier surface.

The starting corresponding substituted salen nickel or zinc complex
10 having a 3-pyridine bridging group may be obtained as described in Catal. Sci. Technol., 2014, 4, 1615, ChemCatChem 2011, 3, 831 – 834. This process is especially suited to prepare a complex having the 3-pyridine bridging group and its corresponding complex having a 3-pyridinium bridging group.

15 In step (a) the corresponding substituted salen nickel or zinc complex is demetallized to obtain a demetallized salen ligand. Demetallation may be performed by known demetallation processes such as for example described in Organometallics 2002, 21, 14, 2950–2957. The demetallation is suitably performed in a water-free demetallation process in the presence of imidazole in
20 acetonitrile, toluene, tetrahydrofuran (THF) or methyl-tetrahydrofuran. This step is performed in a high yield. Tetrahydrofuran (THF) or methyl-tetrahydrofuran are preferred, especially when larger amounts of the complex is prepared.

25 Examples of demetallized salen ligands which after metalation result in a complex according to the invention are illustrated in Figure 1.

In step (b) the demetallized salen ligand of step (a) is contacted with an aluminium compound. This aluminium compound comprises a precursor for group B as used in this description to illustrate the preferred complexes. When
30 B is chloride the aluminium compound is suitably diethylaluminium chloride ($\text{Al}(\text{Et})_2\text{Cl}$) or aluminium diethoxy chloride ($\text{Al}(\text{OEt})_2\text{Cl}$). When B is an alkoxy group, such as ethoxy, the aluminium compound is preferably triethoxy aluminium. When B is an alkyl group the aluminium compound is suitably a

trialkyl aluminium compound, preferably wherein the alkyl group has 1-5 carbon atoms, such as for example trimethyl aluminium and triethyl aluminium.

5 Preferably the aluminium compound is added gradually in step (b) to the demetallized salen ligand as dissolved or dispersed as a slurry in a suitable solvent when the process is performed at a larger scale to enhance the contacting of the reagents. It is found that if the aluminium compound is not added gradually the reaction mass solidifies and effective mixing of the reagents is not possible. The demetallized salen ligand is preferably dissolved
10 or dispersed as a slurry in a suitable solvent, like for example toluene or THF (tetrahydrofuran). The gradual addition is preferably performed for more than 1 hours and preferably more than 1.5 hours. Preferably the addition continues for not more than 3 hours. The temperature is preferably between 20 and 90 °C, more preferably between 50 and 80 °C. Preferably a C5-C10 hydrocarbon
15 alkane solvent, preferably heptane, is added to lower the solubility of the obtained optionally substituted salen aluminium complex. The solidified complex may be separated from the solvents by filtration.

The corresponding optionally substituted salen aluminium complex
20 having a pyridinium bridging group is prepared in a step (b). In step (c) the optionally substituted salen aluminium complex having a pyridine bridge as obtained in step (b) is subjected to an alkylation reaction to obtain the corresponding optionally substituted salen aluminium complex having a pyridinium bridging group. The alkylation is suitably performed by contacting
25 the optionally substituted salen aluminium complex having a pyridine bridge in a suitable solvent with a halogen-R⁸ compound, preferably a bromide compound, Br-R⁸, where R⁸ is the anchoring group as described above. A suitable solvent is tetrahydrofuran (THF), dimethylformamide (DMF), NMP, n-butyl pyrrolidone, sulfolane dimethyl sulfoxide (DMSO) or mixtures of dimethyl
30 sulfoxide (DMSO) and acetonitrile or mixtures of dimethyl sulfoxide (DMSO) and sulfolane or mixtures of dimethyl sulfoxide (DMSO) and n-butyl pyrrolidone.

It has been found advantageous to perform the alkylation starting with the optionally substituted salen aluminium complex instead of alkylating the starting optionally substituted salen zinc complex having a pyridine bridging group. It has been found not possible to subject the zinc complex to the alkylation with a bromide compound, Br-R. Starting with the aluminium complex such an alkylation with Br-R is possible enabling the preparation of the complex of this invention wherein X is a bromide ion.

In step (d) the alkylated optionally substituted salen aluminium complex obtained in step (c) is immobilized on a carrier surface. In this step (d) also the halogen salt and the optional amine are immobilised on the carrier surface. This may be performed by simultaneously contacting the carrier surface with these individual compounds wherein preferably the anchoring groups of these compounds form a covalent bond with the reactive functionalities of the carrier surface. Alternatively the heterogeneous catalyst may be prepared by simultaneously contacting the carrier surface with the salen aluminium complex and the preferred tertiary amine. The resulting heterogeneous precursor catalyst may subsequently be contacted with a halogen compound wherein part of the immobilized tertiary amines react to form the preferred quaternary ammonium halogen salt. This activation of the heterogeneous precursor catalyst may be performed when preparing the heterogeneous catalyst or when one intends to use the catalyst at the process location. This process of obtaining the heterogeneous catalyst has the advantage that no halogen salt is required to be individually immobilised.

The invention is therefore also directed to a heterogeneous precursor catalyst comprising carrier particles having a carrier surface, to which carrier surface a salen aluminium complex and/or its oxo-dimer are immobilized and wherein to which carrier surface a tertiary alkyl amine is immobilized. Preferably the molar ratio of tertiary amine to the atomic aluminium of the salen aluminium complex and/or its oxo-dimer is larger than 3:1 and preferably larger than 4:1. This provides a large presence of immobilised tertiary amines of which part are reacted to the preferred quaternary ammonium halogen salt when activating the

catalyst. Preferably activation is performed such to obtain a heterogeneous catalyst having a molar ratio of amine and total quaternary ammonium, excluding the optional quaternary ammonium as part of the salen aluminium complex, is between 3: 1 and 8: 1.

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The invention is also directed to a process to activate the above heterogeneous precursor catalyst by contacting with a halogen compound and preferably an iodide compound and more preferably a bromide compound. The halogen of the halogen compound is the catalyst system halogen. Examples of
10 suitable halogen compounds are the halogen compounds described below for the process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide.

In the above described heterogeneous catalyst according to this
15 invention embodiments are described wherein an alkylated amine and a quaternary ammonium halogen salt are immobilized. The immobilized quaternary ammonium halogen salt acts as the co-catalyst when the catalyst is used in a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide. For this catalyst the salen aluminium complex
20 may be any as described above and preferably comprising of a quaternary ammonium halogen salt as part of the anchoring group described above. In other embodiments the quaternary ammonium halogen salt which may act as a co-catalyst is part of the anchoring group immobilizing the salen aluminium complex to the carrier surface. The immobilized halogen salt may then be any
25 one of the afore described such as the phosphonium halogen salt and preferably the quaternary ammonium halogen salt.

Thus in the preferred heterogeneous catalyst alkylated amines and quaternary ammonium will be immobilized, wherein the quaternary ammonium
30 may be immobilized as part of the immobilized halogen salt and as part of the immobilized salen aluminium complex. The molar ratio of individually immobilized amine and individually immobilized quaternary ammonium, thus

excluding the optional quaternary ammonium as part of the salen aluminium complex, is preferably between 3: 1 and 8: 1.

5 The molar ratio of the individually immobilised salen aluminium complex as expressed in mol aluminium and the individually immobilised amine is preferably between 1:3 and 1:5. An optimal heterogeneous catalyst has a molar ratio of salen aluminium complex as expressed in mol aluminium, amine and total ammonium, excluding the optional quaternary ammonium as part of the salen aluminium complex, of about 1 mol aluminium, 4 mol amine and 1 mol
10 ammonium. Such a catalyst may be prepared by contacting the carrier with the, to be immobilised separate components of halogen ammonium salt, salen aluminium complex and tertiary amine in about the same ratio's. The ratio's of these compounds on the carrier surface of the heterogeneous catalyst as prepared may be determined by Inductively coupled plasma mass spectrometry
15 (ICP-MS).

 The heterogeneous catalyst may be used as a catalyst or as part of a catalyst in a copolymerisation process to prepare aliphatic polycarbonates starting from an epoxide compound and carbon dioxide. Another reaction
20 where the heterogeneous catalyst may be used is in a process to prepare a polyester by ring-opening polymerisation of a lactone compound as for example described in WO2012/065711.

 Preferably the heterogeneous catalyst is used as a catalyst or as part of
25 a catalyst in a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide.

 The invention is therefore also directed to a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide in the
30 presence of the heterogeneous catalyst.

 Preferably the process is performed in the presence of a corresponding halogen compound. The halogen compound may be an aryl halogen compound

and preferably an alkyl halogen compound. The halogen of the halogen compound is the catalyst system halogen. The presence of the corresponding halogen compound is beneficial for the activity and stability of the catalyst. It has been found that by adapting the content of corresponding halogen compound when performing the process the reaction rate can be influenced. The halogen compound is not a halogen salt. The amount of corresponding halogen compound does not necessarily be high. Good results have been obtained when the corresponding halogen compound is present in between 0.3 and 10 mol% with respect to the epoxide compound, preferably between 0.5 and 3 mol% with respect to the epoxide compound.

When a bromide salt is immobilised preferably a bromide compound is present as the corresponding halogen compound. This bromide compound can in situ react with the immobilized tertiary amines to form the required quaternary ammonium salt. In this manner any immobilised halogen salt which is somehow removed from the carrier surface and which does not act as a co-catalyst can be replaced by in-situ formed immobilised quaternary ammonium salt. When no amines are immobilised as for example in the illustrated gallium-based catalyst it is also advantageous to perform the process in the presence of a halogen compound. This may be explained in that the halogen compound can in-situ repair and deactivated immobilized halogen salt. In this way the level of the co-catalyst can be kept at a desired level at the carrier surface. When the desired bromide salt is used the process is preferably performed in the presence of an aryl bromide and/or an alkyl bromide. Thus re-activation with a tetra-n-butylammonium bromide (TBAB) as in the process of WO2009/109765 can be omitted. A suitable aryl bromide is benzyl bromide. Because this compound is corrosive for some metals it may be preferred to perform the process in glass or glass lined process apparatuses. Preferably less corrosive bromide compounds are used such as alkyl bromide, such as C3-C10 alkyl bromide compounds, for example propyl bromide, butyl bromide, pentyl bromide, hexyl bromide, heptyl bromide and octyl bromide. Another suited group of alkyl bromides are alkyl dibromides, such as 1,2-dibromoethane, 1,3-

dibromopropane, 1,4-dibromobutane, 1,5 dibromopentane and 1,6-dibromohexane.

The starting epoxide compound suitably has 2 to 8 carbon atoms.

5 Suitable epoxide compounds are ethylene oxide, propylene oxide, butylene oxide, pentene oxide, glycidol, styrene oxide, epichlorohydrin or fluoroethylene oxide.

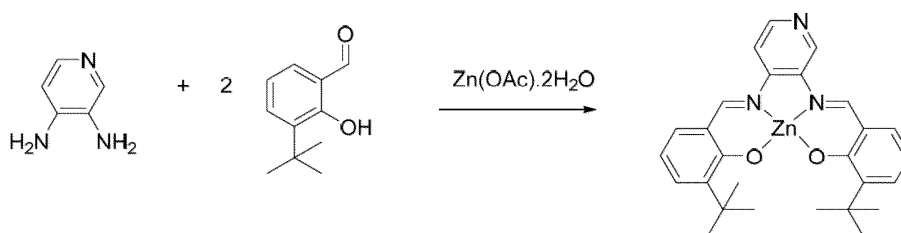
10 The process may be performed as a continuous process wherein the heterogeneous catalyst is present as part of a fixed bed in a fixed bed reactor. The halogen compound may then be co-fed to the fixed bed reactor together with the epoxide and carbon dioxide. Depending on the epoxide and further process conditions the reaction in the fixed bed may be performed in the gas or liquid phase or combinations of gas and liquid phases. The temperature may be
15 between 20 and 150 °C, more preferably between 40 and 120 °C, and the absolute pressure is suitably between 0.1 and 0.5 MPa, more preferably between 0.1 and 0.3 MPa.

20 The carbon dioxide is suitably contacted with the epoxide compound in a suspension of liquid cyclic carbonate and the heterogeneous catalyst. The temperature and pressure conditions are chosen such that the cyclic carbonate is in its liquid state. The temperature and pressure conditions are further chosen such that carbon dioxide and epoxide easily dissolve in the liquid cyclic carbonate reaction medium. The temperature may be between 0 and 200 °C
25 and the pressure between 0 and 5.0 MPa (absolute) and wherein temperature is below the boiling temperature of the cyclic carbonate product at the chosen pressure. At the high end of these temperature and pressure ranges complex reactor vessels will be required. Because favourable results with respect to selectivity and yield to the desired carbonate product are achievable at lower
30 temperatures and pressures it is preferred that the temperature is between 20 and 150 °C, more preferably between 40 and 120 °C, and the absolute pressure is between 0.1 and 0.5 MPa, more preferably between 0.1 and 0.4

MPa. The process may be performed as for example described in WO2021/094447.

Example 1

5 In this example step (a) of the process to prepare the complex according to the invention is illustrated. The preparation of a [Zn(3,4-Py Salphen)] according to the below scheme is described.

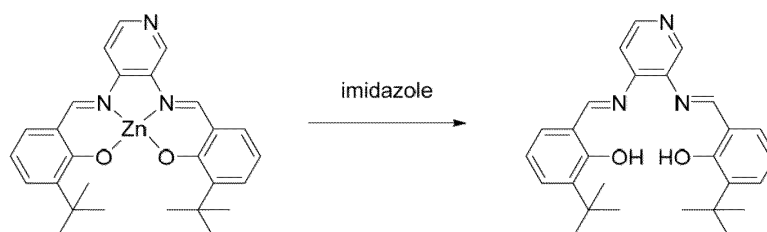


10 A round bottom flask was charged with 3,4-diamine pyridine (1.44 gr. 13.2 mmol), 3-tert butyl salicylaldehyde (4.8 mL, 28.0 mmol), zinc acetate dihydrate (3.08 g, 13.8 mmol), triethyl amine (5.0 mL, 35.9 mmol) in 100 mL methanol. The mixture was stirred and heated to reflux for 24 hours providing a bright red solid. The solid was filtered off and washed with methanol (3 x 20
15 mL). The yield of the [Zn(3,4-Py Salphen)] is 6.24 gram (95.6%).

The product was characterised by ¹H-NMR: ¹H NMR (300 MHz, DMSO-d₆) δ 9.20 (s, 1H), 9.15 (s, 2H), 8.48 (d, J = 5.5 Hz, 1H), 7.88 (d, J = 5.5 Hz, 1H), 7.29 (m, 4H), 6.48 (td, J = 7.5, 3.2 Hz, 2H), 1.48 (s, 18H). The NMR data
20 indicates that the desired product was formed.

Example 2

In this example step (b) of the process to prepare the complex according to the invention is illustrated. The [Zn(3,4-Py Salphen)] as obtained in Example
25 1 is demetallized according to the below scheme.

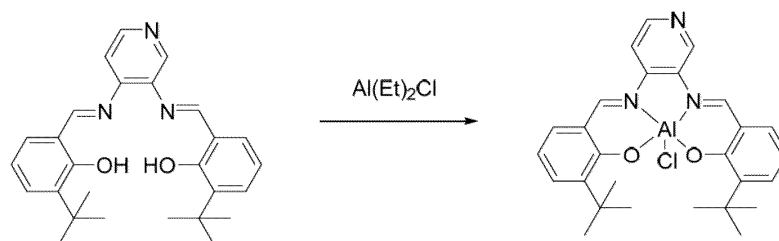


A flask was charge with the [Zn(3,4-Py-Salphen)] (6.24 gram, 12.65 mmol) of Example 1 and dissolved in 60 mL toluene. To this solution, imidazole (3.48 g, 50.6 mmol) was added heated to 60 °C for 2 hours. The solids were filtered off and washed with toluene. The solid again taken up in methanol (60 mL) and heated 60 °C for 2 hours. The solids were filtered off and dried yielding 4.27 grams of an orange powder. Yield 78.6%.

The product was characterised by ¹H-NMR: ¹H NMR (300 MHz, DMSO-d₆) δ 13.80 (s, 1H), 13.73 (s, 1H), 9.07 (d, J = 8.7 Hz, 2H), 8.71 (s, 1H), 8.58 (d, J = 5.3 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.42 (td, J = 8.0, 1.7 Hz, 2H), 6.95 (td, J = 7.7, 3.3 Hz, 2H), 1.38 (s, 18H). The NMR data indicates that the desired product was formed.

Example 3

In this example step (c) of the process to prepare the complex according to the invention is illustrated. The substituted salen aluminium complex having a pyridine bridge is prepared from the demetallized ligand obtained in Example 2 according to the below scheme.



In a flame dried Schlenk, 3,4-Py Salphen ligand (2.6 g. 6.0 mmol) as obtained in Example 2 was dissolved in 24 mL toluene and heated to 60 °C. the

Al(Et)₂Cl (1.8 M in toluene, 6.4 mL, 11.6 mmol) was added and the reaction was stirred for 17 hours. The reaction was cooled down to room temperature and the product was filtered off and washed with toluene (10 mL) and pentane (2 x 10 mL) yielding a yellow solid (1.19 g, 40%).

5

The product was characterised by ¹H-NMR: ¹H NMR (300 MHz, DMSO-d₆) δ 9.50 (s, 1H), 9.44 (d, J = 5.0 Hz, 2H), 8.65 (d, J = 5.6 Hz, 1H), 8.13 (d, J = 5.7 Hz, 1H), 7.57 (td, J = 11.8, 10.6, 4.8 Hz, 4H), 6.90 – 6.75 (m, 2H), 1.56 (d, J = 1.8 Hz, 19H). The NMR data indicates that the desired product was formed.

10

Example 4

The substituted salen aluminium complex (3.68 g, 7.5 mmol) as obtained in Example 3 was loaded into a flame dried Schlenk flask under nitrogen atmosphere. To the Schlenk flask was added dry dimethylformamide (8.4 mL) and 3-bromopropyltrimethoxysilane (5.64 mL, 30 mmol). The reaction mixture was heated to 80°C for 48 hours and yielded an orange precipitate. The reaction was then cooled down to room temperature and centrifuge to isolate the solid which was subsequently washed with 3x10 mL petroleum ether and 3x10 mL diethyl ether to remove the excess 3-bromopropyltrimethoxysilane. The orange powder obtained was dried under vacuum to yield 5 g of the silylated compound with 6 molecules of DMF.

15

20

¹H NMR: (DMSO-d₆) 9.88 (br s, 1H), 9.63 (br s, 1H), 9.53 (br s, 1H), 9.07 (d, 7.00 Hz, 1H), 8.69 (d, 7.00 Hz, 1H), 7.65 (m, 4H), 7.56 (d, 7.6 Hz, 1H), 6.89 (t, 7.59 Hz, 2H), 4.55 (t, 7.20 Hz, 2H), 3.51 (s, 9H, Si-OMe), 2.11 (m, 2H), 1.56 (s, 9H), 1.55 (s, 9H), 0.70 (m, 2 H)

25

Example 5

4 g of Grace Silica (40-63 μm particle size, 35 Å pores) was dried in a baffled flask using a Kugelrohr apparatus at 200 °C and 50 rpm for 15 hours. The silica was cooled down to room temperature and the flask was refilled with nitrogen. 30 mL of propylene carbonate was then added to the silica and the resulting

30

slurry was heated up to 130 °C. The complex, ammonium bromide salt and amine were individually immobilized to the silica surface by adding a solution of silylated chloroaluminum salen as obtained in Example 4 (1.13 mL of a 0.44 M dimethyl formamide solution), a solution of 3-

5 (tributyl)ammoniumpropyltrimethoxysilane bromide (1.2 mL of a 0.5 M acetonitrile solution) and N,N-dimethylaminopropyltrimethoxysilane (540 µL) in 6 mL of propylene carbonate to the silica over 3 hours. At the end of the addition, the addition vessel was washed with 2x5 mL propylene carbonate and the reaction was continued for 18 hours. The reaction mixture was cooled down

10 to room temperature before filtration over glass fibre filter. The solid was washed with 2x30 mL propylene carbonate and 2x30 mL ethyl acetate and dried under vacuum (10 mbar) at 70°C for 2 hours to yield 4.67 g of the catalyst as a yellow powder.

The molar ratio of the individually immobilized salen aluminium complex as expressed in mol aluminium, individually immobilized tertiary amine and total

15 individually immobilized ammonium of the heterogeneous catalyst and determined by ICP-MS was about the ratio of the above referred to starting compounds: 1 mol aluminium, 4 mol amine and 1 mol ammonium also referred to as Ratio of Al/N/N+ (mol) or the ratio of n/k/m (mol). The ammonium in this

20 ratio relates to the ammonium of the 3- (tributyl)ammoniumpropyltrimethoxysilane bromide only.

ICP-MS analysis of the immobilized salen aluminium complex as prepared in this example is provided in the below table 1.

25

Table 1

<u>Al</u>	<u>Amine</u>	<u>Ammonium</u>
<u>1.00</u>	<u>4.11</u>	<u>1.51</u>

Example 6

Example 5 was repeated wherein more ammonium salt was individually

30 immobilized such that the ratio of the starting compounds as expressed as a

molar ratio of the salen aluminium complex as expressed in mol aluminium, mol tertiary amine and mol ammonium was 1 mol aluminium, 4 mol amine and 2 mol ammonium. The ammonium in this ratio relates to the ammonium of the 3-(tributyl)ammoniumpropyltrimethoxysilane bromide only.

5

Example 7

Example 5 was repeated wherein more ammonium salt was individually immobilized such that the ratio of the starting compounds as expressed as a molar ratio of salen aluminium complex as expressed in mol aluminium, mol tertiary amine and mol ammonium was 1 mol aluminium, 4 mol amine and 1.5 mol ammonium. The ammonium in this ratio relates to the ammonium of the 3-(tributyl)ammoniumpropyltrimethoxysilane bromide only.

10

Example 8

In this example the catalytic activity of the heterogeneous catalyst of Examples 5, 6 and 7 were tested in the presence of added octyl bromide in the below reaction of styrene oxide and carbon dioxide to prepare 4-phenyl-1,3-dioxolan-2-one.

15

In a Schlenk reaction flask, 98.06 mg of the heterogeneous catalyst, was heated to 100 °C and put on vacuum. The flask was refilled with CO₂ gas after which the propylene carbonate (3.33 mL), styrene oxide (1 mL) and octyl bromide (30.26 µL) were added. The flask was purged with CO₂ and the stirring was started. After 24 hours the conversion was measured and listed for the different catalysts in Table 2. The main product was 4-phenyl-1,3-dioxolan-2-one.

20

25

Table 2

Catalyst of	Ratio of Al/N/N+ (mol) in preparation	Conversion
Example 5	1:4:1	30.4
Example 6	1:4:2	20.4
Example 7	1:4:1.5	25.5

Example 9

Example 8 was repeated with the catalyst of Example 5 except that the halogen compound was 1,4-dibromobutane (DBB) instead of octyl bromide. The experiment was performed with varying amounts of DBB as listed in Table 3 as Examples 9a-9d. After a first run (Run 1), the stirring was stopped, and the solid catalyst was allowed to settle to the bottom of the Schlenk reaction flask. Thereafter, the solvent phase of the reaction mixture was removed. Then, ethyl acetate (4 mL) was added, the reaction mixture was stirred for 15 minutes before letting the solid catalyst to settle to the bottom of the Schlenk reaction flask. The solvent phase of the reaction mixture was removed. This washing procedure using ethyl acetate was performed twice in total. Then, the Schlenk reaction flask was heated to 100 °C and put on vacuum. The flask was refilled with CO₂ gas after which the propylene carbonate, styrene oxide and the 1,4-dibromobutane (if present) were added. The flask was purged with CO₂ and the stirring was started to repeat the example 8 experiment. After 20 hours the conversion was measured and listed for the different catalysts in Table 3 as Run 2. This was repeated for a Run 3 and Run 4. The results are presented in Table 3. The results indicate an optimal DBB content of around 2 mol% to styrene oxide for the catalyst of Example 5. The presence of DBB enhances the activity of the catalyst and enhances the activity when the catalyst is reused or recycled in subsequent runs when preparing the cyclic carbonate.

Table 3

Example	DBB mol%/StO	Run 1	Run 2	Run 3	Run 4
9a	0	19.6	17.5	16.6	14.7
9b	1	24.8	27.5	29.8	27.5
9c	2	27.3	32.1	32.3	31.3
9d	3	27.9	25.5	25.3	22.3

Example 10

In this example the catalytic activity of the immobilized complex obtained in example 5 is tested in a fixed bed reactor.

In a tubular reactor, 200 mg of pelletized catalyst was supported on top of quartz wool and heated to 100 °C. The Reactor tube was flushed with a CO₂ flow (5 ml/min). A 1,2-propylene oxide flow (50 μl/min) with a small concentration of 1-bromooctane was added to the CO₂ flow (5 ml/min). The flow leaving the reactor tube was cooled using a chiller (3 °C). After the chiller, liquid and gas were separated in a separator. The residual gas was fed to a scrubber. After regular intervals, a sample of the liquid was taken for analysis.

The reactor tube diameter was 10 mm (8 mm internal), The pelletized catalyst size was between 100-300 μm and the content of 1-Bromooctane was 1 mol%.

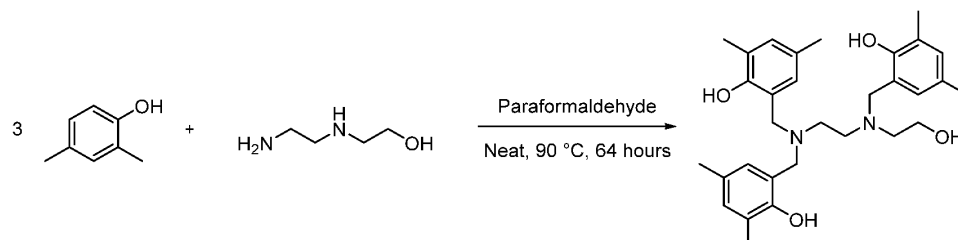
The experiment was run continuously for 20 days. At day 18 and 19 the propylene carbonate (PC) was analyzed in the effluent. The results are listed in Table 4.

Table 4

Sample	Run Time (dd:hh:mm)	PC in effluent (mol%)
1	18:23:48	1.45
2	19:01:46	2.40
3	19:03:32	2.28

Example 11

In this example the process to prepare the ligand to the below scheme is described.



To a 100 mL round bottom, 2,4-dimethylphenol (7.58 g, 62.0 mmol, 3.1 eq),
5 paraformaldehyde (1.80 g, 60.0 mmol, 3.0 eq) and 2-((2-aminoethyl)amino)ethan-1-ol
(2.08 g, 20.0 mmol, 1.0 eq) were added. The reaction was heated to 90 °C resulting
in a light-yellow solution and was allowed to proceed at this temperature for 64 hours
leaving the reaction mixture unchanged. Afterwards, the reaction mixture was cooled
to room temperature and dissolved as a slightly yellow solution in diethyl ether (25
10 mL). To this solution, a generous amount of sodium sulfate was added which was
subsequently filtered off and washed with di-ethyl ether (2 x 5 mL). To the slightly
yellow filtrate, pentane (75 mL) was added leaving the reaction mixture unchanged.
This solution was cooled to -20 °C for 40 hours resulting in a white precipitate in a
slightly yellow solution. This suspension was filtered and washed with ice-cold diethyl
15 ether/ pentane (1:1, 2 times 20 mL) resulting in a white residue and a slightly yellow
filtrate. The residue was dried under reduced pressure at room temperature for 2
hours. The desired product was isolated as a white powder (5.47 g, 54.0 %).

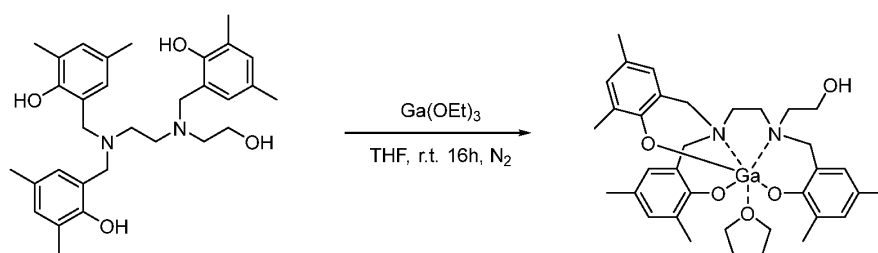
Alternatively, the product can be purified directly after the reaction by column
20 chromatography on silica by eluting with heptane /ethyl acetate/ triethylamine
(80:20:2) until a yellow band comes off followed by eluting with
heptane:isopropanol:triethyl amine (90:10:2).

¹H NMR (300 MHz, DMSO-*d*₆); δ 6.78 (s, 3H, Ar-H), 6.69 (s, 2H, Ar-H), 6.56 (s, 1H,
Ar-H), 3.59 (s, 6H, Ar-CH₂), 3.48 (s, 2H, CH₂OH), 2.68 (s, 2H, CH₂), 2.60 (s, 2H, CH₂),
25 2.48 (s, 2H, CH₂CH₂OH), 2.14 (s, 9H, ArCH₃), 2.09 (s, 6H, ArCH₃), 2.02 (s, 3H, ArCH₃).

^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ 153.01, 152.24, 130.36, 129.94, 127.93, 126.97, 126.71, 126.40, 123.89, 123.42, 122.49, 121.40, 58.12, 57.11, 55.25, 54.92, 49.56, 48.79, 20.13, 16.17, 15.58.

5 Example 12

The preparation of a $[\text{Ga}(\text{trisphenolate})]$ complex according to the below scheme is described.



10

To a 250 mL round bottom Schlenk flask, the trisphenolate ligand (4.96 g, 9.79 mmol, 1.0 eq), gallium(III) ethoxide (2.01 g, 9.79 mmol, 1.0 eq) of Example 11 and pre-dried THF (100 mL) were added resulting in a slightly turbid light yellow solution. The reaction was allowed to proceed at room temperature for 16 hours. The reaction mixture was then filtered over Celite filter aid and washed with pre-dried THF (2 x 15 mL) resulting in a clear slightly yellow solution as the filtrate. Afterwards, the THF was evaporated off under reduced pressure and further dried under reduced pressure at room temperature for 2 hours. The $\text{Ga}(\text{trisphenolate})$ complex was isolated as the THF-adduct being an off-white powder (6.30 g, 99.7 %).

20

^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 7.19 (s, 1H, OH), 6.88 – 6.73 (m, 3H, Ar-H), 6.61 (d, $J = 2.2$ Hz, 1H, Ar-H), 6.56 (d, $J = 2.2$ Hz, 1H, Ar-H), 6.48 (d, $J = 2.2$ Hz, 1H, Ar-H), 4.34 (d, $J = 12.8$ Hz, 1H, CH_2), 4.16 (d, $J = 13.4$ Hz, 1H, CH_2), 3.89 (d, $J = 12.8$ Hz, 1H, CH_2), 3.62 (m, 2H, THF, CH_2O), 3.58 – 3.31 (m, 6H, Ar- CH_2), 3.02 – 2.84 (m, 2H, CH_2), 2.84 – 2.60 (m, 3H CH_2), 2.20 (s, 3H, ArCH_3), 2.14 (t, $J = 5.7$ Hz, 12H, ArCH_3), 1.83 (s, 3H, ArCH_3), 1.76 (m, 2H, THF, CH_2).

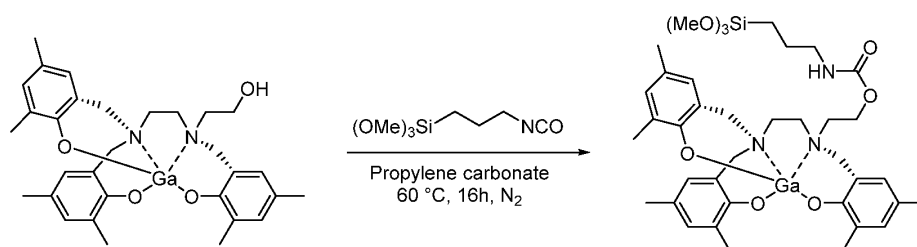
25

^{13}C NMR (75 MHz, DMSO) δ 159.50, 157.87, 130.97, 130.75, 130.46, 127.80, 127.37, 127.10, 126.66, 126.44, 126.17, 123.49, 123.09, 121.96, 121.55, 120.69, 118.08, 67.06 (THF, CH_2O), 61.33, 59.50, 55.70, 53.82, 53.26, 52.19, 25.18 (THF, CH_2), 20.15, 16.93, 16.40, 15.92.

5

Example 13

The preparation of a [Ga(trisphenolate)-propyl(trimethoxy)silane] according to the below scheme is described.



10

Under a nitrogen atmosphere, [Ga(trisphenolate)] (5.45 g, 9.50 mmol, 1.00 eq), (3-isocyanatopropyl)trimethoxysilane (1.95 g, 9.50 mmol, 1.00 eq) of Example 12 and propylene carbonate (19 mL) were added to a 50 mL Schlenk flask resulting in a white suspension. The reaction was allowed to proceed at 60 °C for 16 h resulting in a light brown solution. The reaction mixture was directly used for immobilization.

15

The same reaction can also be performed in pre-dried THF under a nitrogen atmosphere. After the reaction, THF was evaporated off under reduced pressure and the targeted product [Ga(trisphenolate)-propyl(trimethoxy)silane] was isolated as a slightly yellow powder in quantitative yields. NMR data of this compound was obtained in CDCl_3 .

20

^1H NMR (300 MHz, CDCl_3) δ 7.07 – 6.25 (m, 6H, Ar-H), 5.98 (s, 1H, NH), 4.26 (d, J = 13.5 Hz, 1H, CH_2), 3.96 (d, J = 13.5 Hz, 1H, CH_2), 3.74 (m, 2H, CH_2), 3.64 (m, 1H, CH_2), 3.61 – 3.47 (m, 6H, Ar- CH_2), 3.40 (m, 1H, CH_2), 3.19 – 3.01 (m, 2H, CH_2), 2.93 – 2.74 (m, 2H, CH_2), 2.35 – 2.02 (m, 15H, Ar CH_3), 1.92 – 1.80 (m, 3H, Ar- CH_3), 1.71 – 1.57 (m, 1H, CH_2), 1.43 (s, 9H, $\text{Si}(\text{OCH}_3)_3$), 1.31 – 1.16 (m, 1H, CH_2), 0.73 – 0.44 (m, 2H, SiCH_2).

25

¹³C-NMR (75 MHz, CDCl₃) δ 158.58, 157.41 (br), 155.55, 132.08, 131.53, 128.61, 127.69, 126.31, 124.16, 120.88, 116.60, 77.59, 77.16, 76.74, 67.99 (THF, CH₂O), 51.95, 50.58, 43.43, 30.35, 26.95, 25.64 (THF, CH₂), 23.22, 20.41, 16.55, 16.24, 15.76, 8.54, 6.33.

FT-IR (ATR): 1728 cm⁻¹ (s, RNH-C(O)-OR')

Example 14

Under an nitrogen atmosphere, a mixture of [Ga(trisphenolate)-propyl(trimethoxy)silane] of Example 13 N,N-dimethylaminopropyltrimethoxysilane and 3-(tributyl)ammoniumpropyltrimethoxysilane bromide were added to a 50 mL Schlenk flask to a total volume of 18 mL of propylene carbonate (PC) resulting in a slightly yellow solution. The compositions of the (co-)catalyst(s) solutions are listed in Table 5 below.

Table 5

Compositions	Gallium complex (mmol)	Amine (mmol)	Ammonium (mmol)	Molar ratio Ga:N:N+ (n:k:m)
14a	1.5	7.5	0.0	1:5:0
14b	1.5	0.0	7.5	1:0:5
14c	1.5	1.5	6.0	1:1:4
14d	1.5	6.0	1.5	1:4:1

Using a Radleys MYA 4 reaction system equipped with a top stirrer, silica (10 g, SP 540-11508, Grace GmbH, 35 Å, 40-60 μm) was dispersed in propylene carbonate (75 mL) and heated to 130 °C over a period of 45 minutes. Thereafter, a solution consisting of [Ga(trisphenolate)-propyl(trimethoxy)silane] as obtained in Example 13 (3.0 mL of a 0.5 M propylene carbonate solution), 3-(tributyl)ammoniumpropyltrimethoxysilane bromide (12 mL of a 0.5 M acetonitrile solution) and N,N-dimethylaminopropyltrimethoxysilane (328 μL) in 3 mL of propylene carbonate was added over 3 hours using a syringe pump. The reaction mixture was allowed to stir for

an additional 18 hours at 130 °C after which the reaction mixture was cooled to room temperature. The resulting slightly yellow suspension was filtered using a glass fibre filter (Whatman, 1820-055) and washed with propylene carbonate (2 x 20 mL) followed by ethyl acetate (1 x 20 mL) resulting in a slightly yellow powder residue and slightly yellow solution as filtrate. Afterwards, the residue was dried in a vacuum oven at 70 °C at 5 mbar, for 2 hours. This material was used for catalysis as the heterogeneous catalyst 14c. For compositions 14a, 14b and 14d heterogeneous catalysts 14a, 14b and 14d were prepared in a similar manner.

10 Example 15

In this example the catalytic activity of the heterogeneous catalyst 14a-14d obtained in Example 14 were tested in the below reaction of styrene oxide and carbon dioxide to prepare 4-phenyl-1,3-dioxolan-2-one.

15 In a Schlenk reaction flask, 98.06 mg of the heterogeneous catalyst, was heated to 100 °C and put on vacuum. The flask was refilled with CO₂ gas using a balloon at ambient pressure after which the propylene carbonate (3.30 mL) and styrene oxide (1 mL) was added. The flask was purged with CO₂ and the stirring was started. After 20 hours the conversion was measured and listed for the different catalysts in Table 6.

20 The main product was 4-phenyl-1,3-dioxolan-2-one.

Example 16

Example 15 was repeated except that also 1,4-dibromobutane (DBB) was added to the flask. After 20 hours the conversion was measured and listed for the different catalysts and amounts of DBB relative to styrene oxide (StO) in Table 6. The main product was 4-phenyl-1,3-dioxolan-2-one.

Table 6.

Exp. No.	Heterogeneous catalyst	Molar ratio Ga:N:N+ (n:k:m)	Mol% DBB / StO	Conversion (%)
----------	------------------------	-----------------------------	----------------	----------------

15	14a	1:5:0	0	1.84
16	14a	1:5:0	1	12.79
16	14a	1:5:0	2	16.84
15	14b	1:0:5	0	16.92
16	14b	1:0:5	1	30.86
16	14b	1:0:5	2	31.75
15	14c	1:1:4	0	17.67
16	14c	1:1:4	1	29.67
16	14c	1:1:4	2	31.95
15	14d	1:4:1	0	4.26
16	14d	1:4:1	1	13.48
16	14d	1:4:1	2	18.05

Example 17

In this example the catalytic activity of the heterogeneous catalysts used in example 15 and 16 was tested for its recyclability in the reaction of styrene oxide and carbon dioxide to prepare 4-phenyl-1,3-dioxolan-2-one.

After the first run (Run 1), the stirring was stopped, and the solid catalyst allowed to settle to the bottom of the Schlenk reaction flask. Thereafter, the solvent phase of the reaction mixture was removed. Then, ethyl acetate (4 mL) was added, the reaction mixture was stirred for 15 minutes before letting the solid catalyst to settle to the bottom of the Schlenk reaction flask. The solvent phase of the reaction mixture was removed. This washing procedure using ethyl acetate was performed twice in total. Then, the Schlenk reaction flask was heated to 100 °C and put on vacuum. The flask was refilled with CO₂ gas after which the propylene carbonate (3.30 mL), styrene oxide (1 mL) and 1,4-dibromobutane (DBB, 20.92 µL) were added. The flask was purged with CO₂ and the stirring was started. After 20 hours the conversion was measured and listed for the different catalysts in Table 7 as Run 2. The main product was 4-phenyl-1,3-dioxolan-2-one.

Table 7

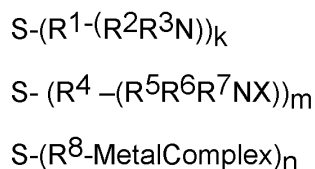
Heterogeneous catalyst	Molar ratio Ga:N:N+	Mol% DBB / StO	Conversion Run 1 (%)	Conversion Run 2 (%)
14a	1:5:0	2	16.84	20.45
14b	1:0:5	2	31.75	34.48
14c	1:1:4	2	31.95	31.35
14d	1:4:1	2	18.05	17.18

CLAIMS

1. A heterogeneous catalyst comprising carrier particles having a carrier surface,
to which carrier surface a metal-complex and a halogen salt is immobilized,
5 wherein the metal-complex and the halogen salt are each individually
immobilized to the carrier surface.
2. The heterogeneous catalyst according to claim 1, wherein an amine is
individually immobilized to the carrier surface.
- 10 3. The heterogeneous catalyst according to claim 2, wherein the amine is a
tertiary amine.
4. The heterogeneous catalyst according to any one of claims 1-3, wherein to the
15 carrier surface a quaternary ammonium iodide salt and/or a phosphonium
iodide salt is immobilized as the halogen salt.
5. The heterogeneous catalyst according to any one of claims 1-3, wherein to the
carrier surface a quaternary ammonium bromide salt and/or a phosphonium
20 bromide salt is immobilized as the halogen salt.
6. The heterogeneous catalyst according to any one of claims 1-5, wherein the
halogen salt is a quaternary ammonium halogen salt.
- 25 7. The heterogeneous catalyst according to any one of claims 1-6, wherein the
carrier particle is a silica, alumina and/or an amorphous silica alumina particle.
8. The heterogeneous catalyst according to claim 7, wherein the silanol groups as
present on the surface of the silica or silica-alumina particle and/or the aluminol
30 groups as present on the surface of the alumina or silica-alumina particle and
wherein the metal-complex, the amine and the bromide salt or a iodide salt are
covalently connected to the carrier surface by an alkyl(trialkoxysilane and/or an
alkyltrichlorosilane anchoring group.

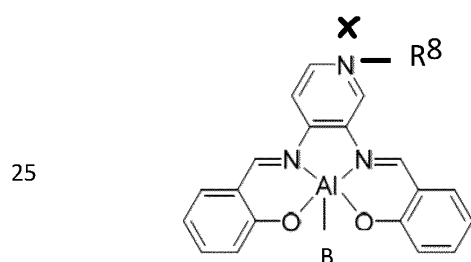
9. The heterogeneous catalyst according to any one of claims 1-8, wherein the metal-complex, tertiary amine and halogen salt are individually immobilized to the carrier surface with respect to each other as presented below:

5



- 10 wherein S is the carrier surface,
 wherein the tertiary amine is $R^1R^2R^3N$ and wherein R^1 is an anchoring group which covalently binds the tertiary amine to the carrier surface S and R^2 and R^3 are the same or different alkyl group having from 1 to 20 carbon atoms or wherein R^2 and R^3 are part of a ring structure forming a 5- or 6 membered ring
 15 or R^2 or R^3 are amino alkyl groups,
 wherein the quaternary ammonium halogen salt is $R^4R^5R^6R^7NX$, wherein X is a bromide or an iodide anion, R^4 is an anchoring group which covalently binds the quaternary ammonium halogen salt to the carrier surface S and R^5 , R^6 and R^7 are the same or different alkyl groups having between 1 and 20 carbon
 20 atoms,
 wherein R^8 is an anchoring group which covalently binds the metal complex to the carrier surface S and
 wherein k may be zero and wherein m:n is the is the molar ratio of the halogen salt and the metal-complex as individually immobilized to the carrier surface S
 25 or when an immobilized amine is present k:m:n is the molar ratio of the amine, the halogen salt and the metal-complex as individually immobilized to the carrier surface S.
10. The heterogeneous catalyst according to claim 7, wherein the metal complex is an aluminium complex and wherein an immobilized amine is present and the
 30 molar ratio of k:m is between 3:1 and 8:1.

11. The heterogeneous catalyst according to any one of claims 9-10, wherein the metal complex is an aluminium complex and wherein the molar ratio of n:k is between 1:3 and 1:10.
- 5 12. The heterogeneous catalyst according to any one of claims 7-9, wherein the silanol groups as present on the surface S of the silica or silica-alumina particle and/or the aluminol groups as present on the surface S of the alumina or silica-alumina particle and wherein R^1 , R^4 and R^8 are the same or different alkyl(trialkoxysilane anchoring group and/or an alkyltrichlorosilane anchoring
- 10 group.
13. The heterogeneous catalyst according to any one of claims 1-12, wherein the metal-complex is an optionally substituted salen aluminium complex having a pyridinium bridging group.
- 15 14. The heterogeneous catalyst according to claim 13, wherein the optionally substituted salen aluminium complex have a 3-pyridinium bridging group.
15. The heterogeneous catalyst according to claim 14, wherein the salen aluminium complex has the following general formula:
- 20



wherein B is a halogen, ethoxy or alkyl group,

- 30 and wherein the phenyl groups of the salen aluminium complex are optionally substituted, where R^8 is an anchoring group connected to the carrier surface and X is a halogen anion.

16. The heterogeneous catalyst according to claim 15, wherein X is an iodide anion or a bromide anion.
17. The heterogeneous catalyst according to any one of claims 15-16, wherein the
5 molar ratio of amine to atomic aluminium of the salen aluminium complex is larger than 3:1 expressed as mol amine: mol atomic aluminium.
18. The heterogeneous catalyst according to any one of claims 15-17, wherein X is
10 bromide and wherein to the carrier surface a quaternary ammonium bromide salt is immobilized as the halogen salt and wherein the molar ratio of amine to the quaternary ammonium bromide salt is between 3:1 and 8:1 mol amine/ mol quaternary ammonium nitrogen.
19. The heterogeneous catalyst according to any one of claims 1-12, wherein the
15 metal of the metal complex is aluminium, gallium, indium, iron, cobalt, nickel, zinc, titanium and/or bismuth.
20. The heterogeneous catalyst according to claim 19, wherein the metal complex
20 is an aminotrisphenolate metal complex.
21. The heterogeneous catalyst according to claim 20, wherein the metal is gallium.
22. Use of the heterogeneous catalyst according to any one of claims 1-21 as a
25 catalyst or as part of a catalyst in a process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide.
23. Use of the heterogeneous catalyst according to claim 22 in the presence of an organic halogen compound.
- 30 24. Use according to claim 23, wherein the organic halogen compound is an aryl halogen compound or an alkyl halogen compound.

25. A process to prepare a cyclic carbonate by reacting an epoxide compound and carbon dioxide in the presence of the heterogeneous catalyst of any one of claims 1-21 and a halogen compound.
- 5 26. The process according to claim 25, wherein the heterogeneous catalyst is present as a suspension in the cyclic carbonate.
27. The process according to claim 25, wherein the heterogeneous catalyst is present as part of a fixed bed in a fixed bed reactor.
- 10 28. The process according to any one of claims 25-27, wherein the halogen compound is an aryl halogen compound or an alkyl halogen compound.
- 15 29. The process according to claim 28, wherein the halogen compound is a C3-C10 alkyl bromide.
30. The process according to claim 29, wherein the alkyl bromide is any one of propyl bromide, butyl bromide, pentyl bromide, hexyl bromide, heptyl bromide, octyl bromide, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5 dibromopentane and 1,6-dibromohexane.
- 20 31. The process according to any one of claims 25-30, wherein the epoxide compound has 2 to 8 carbon atoms.
- 25 32. The process according to claim 31, wherein the epoxide compound is ethylene oxide, propylene oxide, butylene oxide, pentene oxide, glycidol, styrene oxide or fluoroethylene oxide.
- 30 33. A heterogeneous precursor catalyst comprising carrier particles having a carrier surface, to which carrier surface a metal-complex is immobilized and wherein to which carrier surface a tertiary alkyl amine is immobilized.

34. The heterogeneous precursor catalyst according to claim 33, wherein the metal-complex is a salen aluminium complex.
35. The heterogeneous precursor catalyst according to claim 34, wherein the molar ratio of tertiary amine to the atomic aluminium of the salen aluminium complex and/or its oxo-dimer is larger than 3:1 and preferably larger than 4:1.
36. A process to activate a heterogeneous precursor catalyst according to any one of claims 33-35 by contacting the heterogeneous precursor catalyst with a halogen compound.
37. The process according to any claim 36, wherein the halogen compound is an aryl halogen compound or an alkyl halogen compound.
38. The process according to claim 37, wherein the halogen compound is a C3-C10 alkyl bromide.
39. The process according to claim 38, wherein the alkyl bromide is any one of propyl bromide, butyl bromide, pentyl bromide, hexyl bromide, heptyl bromide, octyl bromide, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5 dibromopentane and 1,6-dibromohexane.