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(54) Title: PROCESS FOR REACTIVATING AN AROMATIC CARBONATE CATALYST

(57) Abstract: The invention relates to a process for reactivating a used catalyst, wherein the used catalyst is a homogeneous catalyst comprising titanium, tin or lead and one or more ligands, which has been used in a process for preparing an aromatic carbonate which comprises reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate; and the used catalyst is contacted with an aryl alcohol or an alkyl alcohol in the presence of one or more carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate, wherein the aryl group in the aryl alcohol with which the used catalyst may be contacted is identical to the aryl group in the alkyl aryl carbonate or aryl alcohol used as reactant in said process for preparing an aromatic carbonate; wherein the alkyl group in the alkyl alcohol with which the used catalyst may be contacted is identical to the alkyl group in the dialkyl carbonate or alkyl aryl carbonate used as reactant in said process for preparing an aromatic carbonate; and wherein the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is at least 0.5:1, suitably at least 1:1. The invention also relates to an aromatic carbonate preparation process which includes said catalyst reactivation.



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PROCESS FOR REACTIVATING AN AROMATIC CARBONATE CATALYST

Field of the invention

The present invention relates to a process for reactivating a catalyst that has been used in a process for preparing an aromatic carbonate, to an aromatic carbonate preparation process comprising such catalyst reactivation process, and to a process for making a polycarbonate from a diaryl carbonate prepared in accordance with such aromatic carbonate preparation process.

10 Background of the invention

It is known to produce aromatic carbonates from a dialkyl carbonate and an aryl alcohol. For example, a diaryl carbonate, such as diphenyl carbonate, may be prepared from a dialkyl carbonate and an aryl alcohol. In such process, the dialkyl carbonate is converted into diaryl carbonate via the following steps. In a first step, transesterification of the dialkyl carbonate with the aryl alcohol takes place to yield alkyl aryl carbonate (also an aromatic carbonate) and alkyl alcohol. In a second step, disproportionation of the alkyl aryl carbonate takes place to yield diaryl carbonate and dialkyl carbonate. Further transesterification of the alkyl aryl carbonate with aryl alcohol yielding diaryl carbonate and alkyl alcohol may also take place.

For example, WO2011067263 discloses a process for preparing a diaryl carbonate from a dialkyl carbonate and an aryl alcohol. In said process, three reactive distillation columns are used to complete the conversion of the dialkyl carbonate and the aryl alcohol into the diaryl carbonate.

In general, a catalyst for effecting the above-mentioned chemical reactions may be used. Such catalyst may be homogeneous or heterogeneous. As also disclosed in above-

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mentioned WO2011067263, a suitable catalyst for this is a homogeneous catalyst of formula TiX_4 wherein X may be the same or different and is selected from an alkoxy group, for example an ethoxy group, and an aryloxy group, for example a phenoxy group. Titanium tetraphenoxide, that is to say $Ti(OPh)_4$, is a particularly useful homogeneous catalyst for converting a dialkyl carbonate and an aryl alcohol into a diaryl carbonate, as for example disclosed in US6114564, US20110278174, US8802884 and US20080255336.

However, generally in the course of time, the activity of catalysts such as those as described above decreases.

In above-mentioned WO2011067263, it is disclosed to use three reactive distillation columns in series. Further, it is disclosed therein that in case the bottom stream from the first reactive distillation column comprises catalyst, for example a homogeneous catalyst, no additional catalyst needs to be introduced into the second and third reactive distillation columns. This means that in those second and third reactive distillation columns the same catalyst is used as is used in the first reactive distillation column. The activity of a homogeneous catalyst, like titanium tetraphenoxide, in such process may therefore substantially decrease in the course of time.

In aromatic carbonate production processes, it is desired in order to increase process efficiency, to reuse used catalyst.

For example, in above-mentioned WO2011067263, it is disclosed that a diaryl carbonate and (used) catalyst containing bottom stream from the third reactive distillation column may be subjected to further distillation to obtain pure diaryl carbonate, by introducing said bottom stream into a fourth distillation column from which a top stream comprising diaryl carbonate and a bottom stream comprising

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(used) catalyst and diaryl carbonate are recovered. Further, it is disclosed that the bottom stream from said fourth distillation column (containing used catalyst) may be partially or completely recycled to the first, second or
5 third reactive distillation column. The latter recycle enables reuse of the used catalyst.

Further, for example, EP2540697A1 discloses a method for producing a diaryl carbonate, using a metal-containing catalyst composition as a reaction catalyst, comprising: a
10 step (1) of subjecting a dialkyl carbonate and an aromatic monohydroxy compound to a transesterification reaction so as to obtain an alkylaryl carbonate, and removing an alcohol as by-product from a reaction system; a step (2) of subjecting the alkylaryl carbonate obtained in the step (1) to a
15 transesterification or disproportionation reaction so as to obtain a reaction product including the diaryl carbonate; and a step (3) of distilling the reaction product obtained in the step (2) to separate the reaction product into a low boiling component including the diaryl carbonate and a high boiling
20 component including the reaction catalyst; and a step (4) of recycling the high boiling component separated in the step (3) into the steps (1) and/or (2). Also in this case, the latter recycle enables reuse of the used catalyst.

However, when it is desired to reuse used catalyst in
25 order to increase process efficiency, for example in the aromatic carbonate production processes as taught in above-mentioned WO2011067263 and EP2540697A1, it is also desired to increase the decreased activity of the used catalyst, and preferably to restore the catalyst activity to its original
30 level.

A method for reactivating an aromatic carbonate production catalyst is disclosed in EP1016648A1.

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Above-mentioned EP1016648A1 discloses a process for producing aromatic carbonates from a dialkyl carbonate and an aryl alcohol, using a homogeneous metal-containing catalyst, wherein a high boiling point reaction mixture comprising the catalyst and at least one aromatic carbonate is obtained, which mixture is separated into a product fraction comprising aromatic carbonate and a liquid catalyst fraction comprising the catalyst, which latter fraction is recycled to the reaction system. The invention of EP1016648A1 is characterized in that (i) a portion of said high boiling point reaction mixture and/or (ii) a portion of said liquid catalyst fraction is taken out (split), after which a functional substance (C) is added which may react with the catalyst (B) resulting in a (B)/(C) reaction product, which latter product is recycled to the reaction system directly or indirectly.

In Example 1 of above-mentioned EP1016648A1 (using the system as shown in Figure 1), aromatic carbonate was produced from phenol and dimethyl carbonate in a multi-stage distillation column using a catalyst, which catalyst was previously prepared by reacting lead monoxide with phenol. The bottom stream from said column, containing methyl phenyl carbonate, the (used) catalyst and high boiling point substances, was led into an evaporator. A portion of the resulting evaporation-concentrated liquid, containing the catalyst and high boiling point substances, was recycled to the evaporator and another portion was recycled to the multi-stage distillation column, that is to say without any catalyst reactivation. After a certain period of time, a portion of said evaporation-concentrated liquid was subjected to a multiple-step reactivation procedure which firstly involved leading said liquid into a thin-film evaporator thereby forming an evaporated gas which was recycled. The

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further concentrated liquid originating from said thin-film evaporator and containing the catalyst and high boiling point substances, was then led into a storage vessel. Said further concentrated liquid was then subjected to air oxidation in an electric furnace at a temperature of 700 °C, resulting in formation of lead monoxide as well as other oxidation products (i.e., carbon dioxide, water and low boiling point organic compounds). Said other oxidation products were withdrawn as waste. Then said lead monoxide was reacted with phenol at a temperature of 160 °C in a reaction vessel provided with a distillation column, resulting in lead(II) diphenoxide [Pb(OPh)₂], after which the temperature was increased to 200 °C and water formed by the reaction and unreacted phenol were distilled off from the top of the distillation column. The remaining solution of lead(II) diphenoxide in phenol was finally recycled, via a storage vessel, to the multi-stage distillation column.

The catalyst reactivation method disclosed in above-mentioned EP1016648A1, which in fact comprises a catalyst re-synthesis after an oxidation step, has several disadvantages. A first disadvantage is that only a portion of the catalyst is reactivated, whereas a reactivation method would be desired with which the entire amount of used catalyst could be reactivated and then recycled. A second disadvantage is that the used catalyst containing stream needs to be concentrated in multiple evaporation steps. A third disadvantage is that the catalyst first has to be oxidized (into lead monoxide) using air and applying a high temperature of 700 °C, in order to make it ready for reactivation, after which it is reacted with phenol. A fourth disadvantage is that multiple separations need to be carried out as part of the reactivation procedure, such as to remove waste, as exemplified in Example 1 and Figure 1 of

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EP1016648A1 by the separations resulting in stream 40 (waste oxidation products) and stream 44 (water and unreacted phenol). A fifth disadvantage is that waste is generated, like carbon dioxide, water and low boiling point organic compounds (water is formed both in the oxidation step and during the reaction with phenol), which have to be removed before catalyst recycle. A sixth disadvantage is that solid matter (lead monoxide) is generated, which is cumbersome to handle (more and specialized separation equipment; batch process), which solids handling also results in loss of valuable material (for example on filters).

It is an object of the present invention to provide a simple and efficient process for reactivating a homogeneous catalyst that has been used in a process for preparing an aromatic carbonate, such as a diaryl carbonate, which reactivation process would not have all of the above-discussed disadvantages.

Summary of the invention

Surprisingly it was found that the above-mentioned object may be achieved by contacting the used homogeneous catalyst with an aryl alcohol or an alkyl alcohol in the presence of one or more carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate, wherein the aryl group in the aryl alcohol with which the used catalyst may be contacted is identical to the aryl group in the alkyl aryl carbonate or aryl alcohol used as reactant in said process for preparing an aromatic carbonate; wherein the alkyl group in the alkyl alcohol with which the used catalyst may be contacted is identical to the alkyl group in the dialkyl carbonate or alkyl aryl carbonate used as reactant in said process for preparing an aromatic carbonate; and wherein the molar ratio of the aryl alcohol or alkyl

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alcohol to the carbonates is at least 0.5:1, suitably at least 1:1.

Accordingly, the present invention relates to a process for reactivating a used catalyst, wherein:

5 the used catalyst is a homogeneous catalyst comprising titanium, tin or lead and one or more ligands, which has been used in a process for preparing an aromatic carbonate which comprises reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate,
10 resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate; and

 the used catalyst is contacted with an aryl alcohol or an alkyl alcohol in the presence of one or more carbonates selected from the group consisting of dialkyl carbonate,
15 alkyl aryl carbonate and diaryl carbonate, wherein the aryl group in the aryl alcohol with which the used catalyst may be contacted is identical to the aryl group in the alkyl aryl carbonate or aryl alcohol used as reactant in said process for preparing an aromatic carbonate; wherein the alkyl group
20 in the alkyl alcohol with which the used catalyst may be contacted is identical to the alkyl group in the dialkyl carbonate or alkyl aryl carbonate used as reactant in said process for preparing an aromatic carbonate; and wherein the molar ratio of the aryl alcohol or alkyl alcohol to the
25 carbonates is at least 0.5:1, suitably at least 1:1.

Further, the present invention relates to a process for preparing an aromatic carbonate, comprising:

 reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate in the
30 presence of a homogeneous catalyst comprising titanium, tin or lead and one or more ligands, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate; and

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reactivating the catalyst used in said reaction step in the way as described above for the process for reactivating a used catalyst.

Still further, the present invention relates to a process
5 for making a polycarbonate from a diaryl carbonate prepared in accordance with the aromatic carbonate preparation process of the present invention.

Brief description of the drawings

Figure 1 shows an example of the aromatic carbonate
10 preparation process, comprising a catalyst reactivation step, in accordance with the present invention.

Figure 2 shows another example of the aromatic carbonate preparation process, comprising a catalyst reactivation step, in accordance with the present invention.

15 Detailed description of the invention

While the catalysts used in and processes according to the present invention are described in terms of "comprising", "containing" or "including" one or more various described components and steps, respectively, they can also "consist
20 essentially of" or "consist of" said one or more various described components and steps, respectively.

In the context of the present invention, in a case where a composition (including a catalyst) comprises two or more components, these components are to be selected in an overall
25 amount not to exceed 100%. Further, within the present specification, "substantially no" preferably means that no detectible amount is present.

In the present invention, a catalyst is reactivated which has been used in a process for preparing an aromatic
30 carbonate which comprises reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate. The catalyst to

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be reactivated, which has been used in said aromatic carbonate preparation process, is a homogeneous catalyst comprising titanium, tin or lead and one or more ligands. That is to say, said catalyst comprises titanium, tin or lead
5 as the metal, and one or more ligands coordinated to the metal. Said ligands may be negatively charged. Further, said ligands may be organic. Preferably, said metal is a metal cation. The oxidation state of the metal may vary, but for titanium and tin the oxidation state is preferably +4 whereas
10 for lead the oxidation state is preferably +2. The charge and the number of the one or more ligands are such that this matches the oxidation state of the metal.

The fresh catalyst, from which the used catalyst to be reactivated originates, is also a homogeneous catalyst
15 comprising titanium, tin or lead and one or more ligands, as described above in relation to the used catalyst. Within the present specification, a "fresh catalyst" means a catalyst which has not been used as a catalyst in a chemical process before, in this case the above-mentioned process for
20 preparing an aromatic carbonate comprising reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate.

In said fresh catalyst, said one or more ligands may be selected from the group consisting of a C₁₋₄ alkoxy ligand
25 wherein the alkyl group in said alkoxy ligand has 1 to 4 carbon atoms, and a C₆₋₁₂ aryloxy ligand wherein the aryl group in said aryloxy ligand has 6 to 12 carbon atoms. Preferably, all ligands in the fresh catalyst are either C₁₋₄ alkoxy ligands, preferably identical C₁₋₄ alkoxy ligands, or
30 C₆₋₁₂ aryloxy ligands, preferably identical C₆₋₁₂ aryloxy ligands.

Preferably, the fresh catalyst is of formula M(OR)₄, wherein M = Ti or Sn, most preferably Ti, and R is an alkyl

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group having 1 to 4 carbon atoms, which alkyl group may be the same or different, preferably the same, or of formula $M(OAr)_4$, wherein M is as defined hereinbefore and Ar is an aryl group having 6 to 12 carbon atoms, which aryl group may be the same or different, preferably the same. Alternatively, the fresh catalyst is of formula $Pb(OR)_2$ wherein R is an alkyl group having 1 to 4 carbon atoms, which alkyl group may be the same or different, preferably the same, or of formula $Pb(OAr)_2$ wherein Ar is an aryl group having 6 to 12 carbon atoms, which aryl group may be the same or different, preferably the same.

Thus, the used catalyst to be reactivated in the present invention has been used in a process for preparing an aromatic carbonate which comprises reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate. Therefore, the aromatic carbonate preparation process as described hereinbefore may comprise one or more of the following reactions:

- 1) dialkyl carbonate + aryl alcohol $\rightarrow$ alkyl aryl carbonate + alkyl alcohol (transesterification)
- 2) alkyl aryl carbonate + aryl alcohol $\rightarrow$ diaryl carbonate + alkyl alcohol (transesterification)
- 3) alkyl aryl carbonate + alkyl aryl carbonate $\rightarrow$ dialkyl carbonate + diaryl carbonate (disproportionation)

Preferably, in the above-mentioned fresh catalyst, the alkyl group in the above-mentioned C_{1-4} alkoxy ligand or in the above-mentioned catalysts of formulas $M(OR)_4$ and $Pb(OR)_2$ is the same. Further, preferably, said alkyl group has 1 to 3 carbon atoms. Still further, preferably, said alkyl group is selected from the group consisting of methyl, ethyl, n-propyl and isopropyl, more preferably from the group consisting of

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ethyl, n-propyl and isopropyl, even more preferably from the group consisting of ethyl and isopropyl. Most preferably, said alkyl group is ethyl. A particular suitable example of the fresh catalyst is titanium tetraethoxide of formula
5 $\text{Ti}(\text{OEt})_4$. Generally, it is preferred that said alkyl group is identical to the alkyl group of the dialkyl carbonate or alkyl aryl carbonate used as reactant in the above-mentioned aromatic carbonate preparation process wherein that catalyst is used. If said alkyl group is n-propyl, the oxygen atom is
10 bonded to the first, primary carbon atom of the propyl group. If said alkyl group is isopropyl, the oxygen atom is bonded to the second, secondary carbon atom of the propyl group.

Preferably, in the above-mentioned fresh catalyst, the aryl group in the above-mentioned C_{6-12} aryloxy ligand or in
15 the above-mentioned catalysts of formulas $\text{M}(\text{OAr})_4$ and $\text{Pb}(\text{OAr})_4$ is the same. Further, preferably, said aryl group has 6 to 10 carbon atoms, more preferably 6 to 8 carbon atoms. Most preferably, said aryl group is phenyl. A particular suitable example of the fresh catalyst is titanium tetraphenoxide of
20 formula $\text{Ti}(\text{OPh})_4$. Generally, it is preferred that said aryl group is identical to the aryl group of the alkyl aryl carbonate or aryl alcohol used as reactant in the above-mentioned aromatic carbonate preparation process wherein that catalyst is used.

25 In the present catalyst reactivation process, the used catalyst is contacted with an aryl alcohol or an alkyl alcohol, preferably with an aryl alcohol.

In the present invention, the aryl group in the aryl alcohol with which the used catalyst may be contacted is
30 identical to the aryl group of the alkyl aryl carbonate or aryl alcohol used as reactant in the above-mentioned aromatic carbonate preparation process wherein the catalyst has been used. Said aryl alcohol may be of formula Ar-OH wherein Ar is

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an aryl group having 6 to 12 carbon atoms, preferably 6 to 10 carbon atoms, more preferably 6 to 8 carbon atoms.

Preferably, said aryl alcohol is phenol.

Further, in the present invention, the alkyl group in the
5 alkyl alcohol with which the used catalyst may be contacted is identical to the alkyl group of the dialkyl carbonate or or alkyl aryl carbonate used as reactant in the above-mentioned aromatic carbonate preparation process wherein the catalyst has been used. Said alkyl alcohol may be of formula
10 R-OH wherein R is an alkyl group having 1 to 4 carbon atoms, preferably 1 to 3 carbon atoms. Preferably, said alkyl group is selected from the group consisting of methyl, ethyl, n-propyl and isopropyl, more preferably from the group consisting of ethyl, n-propyl and isopropyl, even more
15 preferably from the group consisting of ethyl and isopropyl. Most preferably, said alkyl alcohol is ethanol.

Further, in the present catalyst reactivation process, the used catalyst is contacted with the above-mentioned aryl alcohol or alkyl alcohol in the presence of one or more
20 carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate, preferably alkyl aryl carbonate and diaryl carbonate. The alkyl group in the dialkyl carbonate and alkyl aryl carbonate may have 1 to 4, suitably 1 to 3 carbon atoms. Suitably, said
25 alkyl group is a methyl group or ethyl group, more suitably an ethyl group. Further, the aryl group in the alkyl aryl carbonate and diaryl carbonate may have 6 to 12 carbon atoms, suitably 6 to 10 carbon atoms, more suitably 6 to 8 carbon atoms. Preferably, said aryl group is a phenyl group.
30 Suitably, the diaryl carbonate may be diphenyl carbonate. Suitable examples of said alkyl aryl carbonate are methyl phenyl carbonate and ethyl phenyl carbonate. Preferably, said dialkyl carbonate is of formula ROC(=O)OR' , wherein R and R'

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may be the same or different and are C₁₋₄ alkyl groups, preferably C₁₋₃ alkyl groups. More preferably, said dialkyl carbonate is dimethyl carbonate or diethyl carbonate, most preferably diethyl carbonate. Preferably, the used catalyst
5 is dissolved in said one or more carbonates.

Still further, in the present catalyst reactivation process, the molar ratio of the above-mentioned aryl alcohol or alkyl alcohol to the above-mentioned carbonates is at least 0.5:1, suitably at least 1:1. In relation to said molar
10 ratio, "carbonates" refers to the total molar amount of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate. Suitably, said molar ratio requirement may relate to that stage where contacting of the used catalyst with the aryl alcohol or alkyl alcohol is started. Said molar ratio is at
15 least 0.5:1 and may suitably be at least 0.6:1, or at least 0.8:1, or at least 1:1, or at least 1.2:1, or at least 1.5:1, or at least 1.7:1, or at least 2:1, or at least 2.5:1, or at least 3:1, or at least 4:1, or at least 5:1, or at least 10:1, or at least 20:1. An upper limit for said molar ratio
20 is not essential. That is to say, the aryl alcohol or alkyl alcohol may be used in a very large molar excess over the carbonates. For example, said molar ratio may be as high as 5,000:1. Thus, suitably, said molar ratio may be at most 5,000:1, or at most 2,000:1, or at most 1,000:1, or at most
25 500:1, or at most 300:1, or at most 200:1, or at most 100:1, or at most 75:1. Accordingly, for example, said molar ratio may range of from 2:1 to 5,000:1 or of from 2:1 to 1,000:1 or of from 2:1 to 300:1. Further, for example, said molar ratio may range of from 4:1 to 5,000:1 or of from 4:1 to 1,000:1 or
30 of from 4:1 to 300:1.

It has surprisingly appeared that by contacting the above-described aryl alcohol or alkyl alcohol with the above-mentioned used catalyst, in a case where one or more

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carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate are present in such amount that the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is at least 0.5:1, suitably at least 1:1, the decreased activity of the used catalyst in an aromatic carbonate preparation process comprising reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, is increased and may be restored to its original level to a large extent, that is to say to the level of activity of fresh catalyst.

Further, in the present catalyst reactivation process, the above-mentioned molar ratio of the aryl alcohol or alkyl alcohol to the carbonates may be of from 0.5:1 to 3.7:1. It has surprisingly appeared that also in case the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is relatively low, for example falling within said range of 0.5:1 to 3.7:1, the decreased activity of the used catalyst in an aromatic carbonate preparation process comprising reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, is still increased and may still be restored to its original level to a large extent, that is to say to the level of activity of fresh catalyst. In such case, said molar ratio is at least 0.5:1 and may suitably be at least 0.6:1, or at least 0.8:1, or at least 1:1, or at least 1.2:1, or at least 1.5:1, or at least 1.7:1, or at least 2:1, or at least 2.5:1, or at least 3:1. Further, in such case, said molar ratio is at most 3.7:1 and may suitably be at most 3.6:1, or at most 3.5:1, or at most 3.2:1, or at most 3:1, or at most 2.5:1, or at most 2:1, or at most 1.5:1. Accordingly, for example, said molar ratio in such case may range of from 0.5:1 to 3.5:1 or of from 0.8:1 to 3:1 or of from 1:1 to 2.5:1.

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Furthermore, the present invention results in the following advantages, especially as compared to the catalyst reactivation method disclosed in above-mentioned EP1016648A1. A first advantage is that the entire amount of used catalyst
5 may be reactivated and then recycled. A second advantage is that any used catalyst containing stream need not be concentrated in multiple evaporation steps. Said stream as such may be subjected to the present reactivation process directly, without performing any separation. A third
10 advantage is that the used catalyst does not first have to be oxidized in order to make it ready for reactivation. Thus, advantageously, no additional feedstock material, such as oxygen, is required. A fourth advantage is that no multiple separations need to be carried out. For example, the aryl
15 alcohol or alkyl alcohol may simply be added to a stream containing the used catalyst, thereby reactivating the catalyst in-situ and not necessarily in a separate, dedicated reactivation unit, after which said stream may be recycled directly, without performing any separation. Thus,
20 advantageously, the present invention need not be performed in batch mode. A fifth advantage is that no or substantially no waste is generated, like carbon dioxide, water and low boiling point organic compounds. A sixth advantage is that no solid matter (solid catalyst) is generated, since during
25 reactivation the used homogeneous catalyst may remain dissolved. Reference is also made to the above introduction where disadvantages of said EP1016648A1 are discussed.

A further advantage is that since the aryl group in the aryl alcohol is identical to the aryl group in the alkyl aryl
30 carbonate or aryl alcohol from the aromatic carbonate preparation process, and the alkyl group in the alkyl alcohol is identical to the alkyl group in the dialkyl carbonate or alkyl aryl carbonate from said aromatic carbonate preparation

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process, no new chemicals are introduced into said aromatic carbonate preparation process after directly recycling the catalyst that has been reactivated with said aryl alcohol or alkyl alcohol. Thus, advantageously, said aryl alcohol or alkyl alcohol need not be removed before recycling the reactivated catalyst.

Still further, in addition to reactivating the used catalyst, another advantage of the present invention is that by adding the aryl alcohol or alkyl alcohol, the melting point of a stream containing both the used catalyst and the above-mentioned one or more carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate, may be lowered at the same time. This advantageously results in less heat being required to keep said stream liquid at the same outside temperature, so that the pumpability of said stream is increased and substantially no solidification within and therefore no plugging of the line transporting such stream can occur. Further, keeping the heating duty the same, by adding the aryl alcohol or alkyl alcohol in the present invention, the catalyst could be reactivated and transported at the same time in liquid form at a relatively low outside temperature. For example, it has appeared that adding 10 moles of phenol per mole of titanium (from the used catalyst) to a stream containing 31 wt.% of used catalyst (containing titanium and ligands, and originating from a process for making diphenyl carbonate from diethyl carbonate and phenol), 68 wt.% of diphenyl carbonate and 1 wt.% of ethyl phenyl carbonate, the melting point of the stream was significantly reduced, from 120 °C to 90 °C. Adding 20 and 40 moles of phenol, resulted in an even greater melting point reduction, to 75 °C and 65 °C, respectively.

The time period during which the aryl alcohol or alkyl alcohol and the used catalyst may be contacted in the

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catalyst reactivation process of the present invention may vary within wide ranges. Said time period may mean the time period between the time at which contacting the used catalyst with the aryl alcohol or alkyl alcohol is started and the
5 time at which reuse of the reactivated catalyst is started in an aromatic carbonate preparation process comprising reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, for example the time at which the reactivated catalyst is introduced into a reactor
10 in which such aromatic carbonate preparation process takes place. Said time period should be at least such that the desired extent of catalyst reactivation is achieved. For example, said time period may be such that at least 50%, or at least 60%, or at least 70%, or at least 80% of the
15 original catalyst activity (activity of fresh catalyst) is restored. Said time period depends on the below-described molar ratio of the aryl alcohol or alkyl alcohol to metal from the catalyst. The higher said molar ratio, the shorter said time period may be in order to restore catalyst activity
20 to a particular level. Further, said time period depends on the below-described temperature within said time period. The higher said temperature, the shorter said time period may be in order to restore catalyst activity to a particular level. Still further, it is envisaged that said time period may
25 extend until after the catalyst has already been reactivated. For example, the used catalyst and the aryl alcohol or alkyl alcohol may be contacted in a storage vessel for multiple days or even longer, that is to say longer than needed to achieve the desired reactivation. Thus, in the present
30 invention, said time period may for example be of from 1 second to 10 days. Suitably, said time period may be at least 1 second, or at least 10 seconds, or at least 30 seconds, or at least 1 minute, or at least 5 minutes, or at least 10

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minutes, or at least 15 minutes. Further, suitably, said time period may be at most 10 days, or at most 5 days, or at most 1 day, or at most 10 hours, or at most 5 hours, or at most 1 hour, or at most 30 minutes. Thus, for example, said time
5 period may be of from 1 second to 10 days or 30 seconds to 5 days or 1 minute to 1 day or 5 minutes to 10 hours.

The temperature during contacting the used catalyst with the aryl alcohol or alkyl alcohol in the catalyst reactivation process of the present invention may be of from
10 100 to 400 °C, preferably 120 to 240 °C, more preferably 140 to 230 °C, most preferably 160 to 220 °C. Suitably, said temperature may be at least 100 °C, or at least 120 °C, or at least 140 °C, or at least 160 °C. Further, suitably, said temperature may be at most 400 °C, or at most 350 °C, or at
15 most 300 °C, or at most 250 °C, or at most 240 °C, or at most 230 °C, or at most 220 °C. Said temperature may be the same as the temperature in the aromatic carbonate preparation process from which the used catalyst originates.

Preferably, the amount of the aryl alcohol or alkyl
20 alcohol to be contacted with the used catalyst in the catalyst reactivation process of the present invention is such that the alcohol is in molar excess over the metal from the catalyst. Suitably, the molar ratio of alcohol to metal from the catalyst is at least 1:1, or at least 2:1, or at
25 least 3:1, or at least 5:1, or at least 7:1, or at least 10:1. An upper limit for said molar ratio is not essential. That is to say, the aryl alcohol or alkyl alcohol may be used in a very large molar excess over the metal from the catalyst. For example, said molar ratio may be as high as
30 500:1. Thus, suitably, said molar ratio may be at most 500:1, or at most 400:1, or at most 300:1, or at most 200:1. Thus, said molar ratio may be of from 1:1 to 500:1 or 3:1 to 500:1 or 5:1 to 500:1.

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Further, the molar ratio of said one or more carbonates to metal from the catalyst in the catalyst reactivation process of the present invention may vary within wide ranges. Suitably, said molar ratio may be at least 0.5:1, or at least 1:1, or at least 2:1, or at least 3:1, or at least 5:1. Further, suitably, said molar ratio may be at most 100:1, or at most 75:1, or at most 50:1, or at most 25:1, or at most 10:1. Thus, said molar ratio may be of from 1:1 to 100:1 or 2:1 to 50:1 or 3:1 to 25:1.

It is preferred that between (1) use of the catalyst in the above-mentioned aromatic carbonate preparation process and (2) reactivating the used catalyst in accordance with the catalyst reactivation process of the present invention, the used catalyst is not subjected to any treatment that chemically modifies the catalyst, such as for example an oxidation treatment as for example is disclosed in above-mentioned EP1016648A1.

Further, preferably, the catalyst reactivation process of the present invention is carried out separately from the above-mentioned aromatic carbonate preparation process and before any recycle of the catalyst to that process.

The present invention does not only relate to the above-described catalyst reactivation process, but also to a process for preparing an aromatic carbonate, comprising reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate, which process includes said catalyst reactivation process as a step.

Thus, the present invention also relates to a process for preparing an aromatic carbonate, comprising:

reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate in the

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presence of a homogeneous catalyst comprising titanium, tin or lead and one or more ligands, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate; and

5 contacting the catalyst used in said reaction step with an aryl alcohol or an alkyl alcohol in the presence of one or more carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate, wherein the aryl group in the aryl alcohol with which the used
10 catalyst may be contacted is identical to the aryl group in the alkyl aryl carbonate or aryl alcohol used as reactant in said reaction step; wherein the alkyl group in the alkyl alcohol with which the used catalyst may be contacted is identical to the alkyl group in the dialkyl carbonate or
15 alkyl aryl carbonate used as reactant in said reaction step; and wherein the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is at least 0.5:1, suitably at least 1:1.

 The catalyst reactivation step of the above-mentioned
20 aromatic carbonate preparation process corresponds to the above-described catalyst reactivation process of the present invention. The embodiments and preferences as described above with reference to said catalyst reactivation process as such also apply to such catalyst reactivation step of the aromatic
25 carbonate preparation process of the present invention.

 The reaction step of the aromatic carbonate preparation process of the present invention is carried out in the presence of a homogeneous catalyst comprising titanium, tin or lead and one or more ligands. The latter catalyst may be
30 the fresh catalyst as described above in relation to the above-described catalyst reactivation process of the present invention.

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In the aromatic carbonate preparation process of the present invention, the alkyl group in the dialkyl carbonate and alkyl aryl carbonate may have 1 to 4, suitably 1 to 3 carbon atoms. Suitably, said alkyl group is a methyl group or
5 ethyl group, more suitably an ethyl group. Further, in the aromatic carbonate preparation process of the present invention, the aryl group in the aryl alcohol, alkyl aryl carbonate and diaryl carbonate may have 6 to 12 carbon atoms, suitably 6 to 10 carbon atoms, more suitably 6 to 8 carbon
10 atoms. Preferably, said aryl group is a phenyl group. Therefore, preferably, said aryl alcohol is phenol and said diaryl carbonate is diphenyl carbonate. Suitable examples of said alkyl aryl carbonate are methyl phenyl carbonate and ethyl phenyl carbonate. Preferably, said dialkyl carbonate is
15 of formula $\text{ROC}(=\text{O})\text{OR}'$, wherein R and R' may be the same or different and are C_{1-4} alkyl groups, preferably C_{1-3} alkyl groups. More preferably, said dialkyl carbonate is dimethyl carbonate or diethyl carbonate, most preferably diethyl carbonate. Further, preferably, in the aromatic carbonate
20 preparation process of the present invention, a dialkyl carbonate is reacted with an aryl alcohol resulting in the corresponding alkyl aryl carbonate.

To complete the conversion of a dialkyl carbonate and an aryl alcohol into a diaryl carbonate through the intermediate
25 formation of an alkyl aryl carbonate, a series of two or three, preferably three, reactive distillation columns in total may be applied. The various embodiments as disclosed in above-mentioned WO2011067263, disclosing a process wherein three reactive distillation columns are used, may be applied
30 to the present aromatic carbonate preparation process. Within the present specification, a "reactive distillation column" is a distillation column containing a catalyst for effecting a chemical reaction in the distillation column. The

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disclosure of WO2011067263 is herein incorporated by reference.

The pressures in said three reactive distillation columns may vary within wide limits. The pressure at the top of the first reactive distillation column may be 2 to 7 bar, preferably 2.5 to 5 bar. The pressure at the top of the second reactive distillation column may be 0.1 to 3 bar, preferably 0.3 to 1.5 bar. The pressure at the top of the third reactive distillation column may be 10 to 600 mbar, preferably 20 to 500 mbar. Preferably, the pressure at the top of the first reactive distillation column is higher than that of the second reactive distillation column which in turn is higher than that of the third reactive distillation column.

The temperatures in said three reactive distillation columns may also vary within wide limits. The temperature at the bottom of the first, second and third reactive distillation columns may be 50 to 350 °C, preferably 120 to 280 °C, more preferably 150 to 250 °C, most preferably 160 to 240 °C.

The catalyst in one or more of said three reactive distillation columns is the above-described homogeneous catalyst. In addition, a heterogeneous catalyst may be used, especially in the first of these reactive distillation columns.

The aromatic carbonate preparation process of the present invention may be carried out as a batch process, semi-continuous process or continuous process, preferably as a continuous process. Further, the used catalyst may be subjected completely or partially, preferably completely, to the catalyst reactivation step.

Preferably, the catalyst reactivation step and the aromatic carbonate preparation step of the aromatic carbonate

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preparation process of the present invention are carried out separately from each other. Further, preferably, said catalyst reactivation step is carried out before optionally recycling the catalyst to said aromatic carbonate preparation

5 step. Said catalyst reactivation step may be carried out, partially or completely, in a line in which the catalyst is recycled to said aromatic carbonate preparation step, preferably by adding the aryl alcohol or an alkyl alcohol to that line. In such a case, contacting the used catalyst with

10 the aryl alcohol or an alkyl alcohol is effected by inline mixing (mixing in the line). In addition, at least a portion of the catalyst in the line may be fed to a separate vessel, for example a buffer vessel or storage vessel, wherein the catalyst is contacted with the aryl alcohol or alkyl alcohol,

15 which alcohol may be added to said vessel directly or to the line prior to entering said vessel. Such vessel may be provided with mixing means. Using such vessel, optionally provided with mixing means, may advantageously lengthen the time period during which the catalyst and the aryl alcohol or

20 alkyl alcohol are contacted, which in turn may result in a greater catalyst reactivation. Another way to ensure such relatively long contact time period is to add the aryl alcohol or alkyl alcohol to said recycle line at a position which is close to the point where the catalyst leaves the

25 aromatic carbonate preparation step and subsequently enters said recycle line. Still further, another way to ensure such relatively long contact time period is to extend said recycle line, for example by means of a coil configuration.

The present aromatic carbonate preparation process may

30 comprise:

reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate in the presence of a homogeneous catalyst comprising titanium, tin

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or lead and one or more ligands, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate, as described above;

separating the resulting reaction mixture into a first
5 low boiling point fraction and a first high boiling point fraction, wherein the first high boiling point fraction comprises aromatic carbonate and the used catalyst;

optionally separating the first high boiling point fraction comprising aromatic carbonate and the used catalyst
10 into a second low boiling point fraction comprising aromatic carbonate and a second high boiling point fraction comprising aromatic carbonate and the used catalyst;

contacting the used catalyst, partially or completely, from the first or second high boiling point fraction with an
15 aryl alcohol or an alkyl alcohol in the presence of one or more carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate, wherein the aryl group in the aryl alcohol with which the used catalyst may be contacted is identical to the aryl group in
20 the alkyl aryl carbonate or aryl alcohol used as reactant in said reaction step; wherein the alkyl group in the alkyl alcohol with which the used catalyst may be contacted is identical to the alkyl group in the dialkyl carbonate or alkyl aryl carbonate used as reactant in said reaction step;
25 and wherein the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is at least 0.5:1, suitably at least 1:1, as described above, resulting in a mixture comprising aromatic carbonate, reactivated catalyst and aryl alcohol or alkyl alcohol;

30 optionally separating the mixture comprising aromatic carbonate, reactivated catalyst and aryl alcohol or alkyl alcohol into a third low boiling point fraction comprising aryl alcohol or alkyl alcohol and optionally aromatic

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carbonate and a third high boiling point fraction comprising aromatic carbonate and reactivated catalyst; and

optionally using reactivated catalyst from the mixture comprising aromatic carbonate, reactivated catalyst and aryl alcohol or alkyl alcohol or reactivated catalyst from the third high boiling point fraction in reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, preferably in said reaction step after recycling the reactivated catalyst to that reaction step.

In a case where in the above-mentioned reaction step, dialkyl carbonate is reacted with an aryl alcohol, resulting in alkyl aryl carbonate and alkyl alcohol, the above-mentioned first low boiling point fraction comprises alkyl alcohol, any unconverted dialkyl carbonate and optionally any unconverted aryl alcohol and the above-mentioned first high boiling point fraction comprises any unconverted aryl alcohol, alkyl aryl carbonate and the used catalyst. Said first high boiling point fraction may be subjected to a further reaction step wherein alkyl aryl carbonate is converted (by disproportionation) into dialkyl carbonate and diaryl carbonate, after which the resulting reaction mixture may be separated into a first low boiling point fraction and a first high boiling point fraction, as described above and below.

In a case where in the above-mentioned reaction step, alkyl aryl carbonate is reacted with alkyl aryl carbonate (disproportionation), resulting in dialkyl carbonate and diaryl carbonate, the above-mentioned first low boiling point fraction comprises dialkyl carbonate and the above-mentioned first high boiling point fraction comprises diaryl carbonate, any unconverted alkyl aryl carbonate and the used catalyst.

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In particular, the present aromatic carbonate preparation process may comprise:

- (a) introducing dialkyl carbonate, aryl alcohol and a homogeneous catalyst comprising titanium, tin or lead and one or more ligands into a first reactive distillation column;
- (b) recovering from the first reactive distillation column a top stream comprising dialkyl carbonate and alkyl alcohol and a bottom stream comprising alkyl aryl carbonate, aryl alcohol, dialkyl carbonate and catalyst;
- (c) introducing the bottom stream from the first reactive distillation column into a second reactive distillation column;
- (d) recovering from the second reactive distillation column a top stream comprising dialkyl carbonate and aryl alcohol and a bottom stream comprising diaryl carbonate, alkyl aryl carbonate, catalyst and optionally aryl alcohol;
- (e) optionally introducing the bottom stream comprising diaryl carbonate, catalyst, alkyl aryl carbonate and aryl alcohol from the second reactive distillation column into a third reactive distillation column;
- (f) optionally recovering from the third reactive distillation column a top stream comprising aryl alcohol and a bottom stream comprising diaryl carbonate, alkyl aryl carbonate and catalyst and;
- (g) introducing the bottom stream from the second or third reactive distillation column into a fourth reactive distillation column;
- (h) recovering from the fourth reactive distillation column a top stream comprising diaryl carbonate and a bottom stream comprising diaryl carbonate and used catalyst;
- (i) contacting the used catalyst from the bottom stream from the fourth distillation column, partially or completely, with an aryl alcohol or an alkyl alcohol in the presence of

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carbonates which comprise diaryl carbonate from the bottom stream from the fourth distillation column, wherein said aryl alcohol is identical to the aryl alcohol introduced into the first reactive distillation column, said alkyl alcohol is
5 identical to the alkyl alcohol recovered from the first reactive distillation column and wherein the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is at least 0.5:1, suitably at least 1:1, resulting in a stream comprising diaryl carbonate, reactivated catalyst and aryl
10 alcohol or alkyl alcohol;

(j) optionally recycling reactivated catalyst from the stream comprising diaryl carbonate, reactivated catalyst and aryl alcohol or alkyl alcohol resulting from step (i) to the first reactive distillation column or, preferably, to the
15 second reactive distillation column.

The used catalyst should be reactivated in above-mentioned step (i) by contacting with the aryl alcohol or alkyl alcohol before the catalyst is optionally recycled to the first or second reactive distillation column.

20 In a case where catalyst is recycled to the first or second reactive distillation column, such recycle may be performed by introducing a catalyst containing stream directly into said first or second reactive distillation column. Further, in a case where catalyst is recycled to the
25 first reactive distillation column, said catalyst containing stream may be introduced into a line by which dialkyl carbonate or aryl alcohol is introduced into the first reactive distillation column. Preferably, said catalyst containing stream is introduced into a line by which aryl
30 alcohol is introduced into the first reactive distillation column. Still further, in a case where catalyst is recycled to the second reactive distillation column, said catalyst containing stream may be introduced into a line by which the

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bottom stream from the first reactive distillation column is introduced into the second reactive distillation column.

The aryl alcohol or alkyl alcohol to be contacted with the used catalyst in above-mentioned step (i), may be fresh
5 aryl alcohol or fresh alkyl alcohol. Further, said aryl alcohol or alkyl alcohol may be aryl alcohol or alkyl alcohol recovered in any one of above-mentioned steps (b), (d) and (f). Said alkyl alcohol may be alkyl alcohol recovered in above-mentioned step (b), in particular alkyl alcohol from
10 the top stream from the first reactive distillation column, as further described below. Further, said aryl alcohol may be aryl alcohol recovered in any one of above-mentioned steps (d) and (f), in particular aryl alcohol from the top stream from the second reactive distillation column or aryl alcohol
15 from the top stream from the second reactive distillation column, preferably aryl alcohol recovered in above-mentioned step (d), as further described below.

Further, the aryl alcohol or alkyl alcohol to be contacted with the used catalyst in above-mentioned step (i),
20 may be added to the bottom stream comprising diaryl carbonate and used catalyst from the fourth reactive distillation column, before any catalyst recycle. Alternatively or additionally, in a case where catalyst is recycled to the first reactive distillation column, said aryl alcohol or
25 alkyl alcohol may be introduced into a line by which dialkyl carbonate or aryl alcohol, preferably aryl alcohol, is introduced into the first reactive distillation column, provided that the bottom stream comprising diaryl carbonate and used catalyst from the fourth reactive distillation is
30 also introduced into said line. Further, alternatively or additionally, in a case where catalyst is recycled to the second reactive distillation column, said aryl alcohol or alkyl alcohol may be introduced into a line by which the

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bottom stream from the first reactive distillation column is introduced into the second reactive distillation column, provided that the bottom stream comprising diaryl carbonate and used catalyst from the fourth reactive distillation is also introduced into said line.

Further, in the above-described aromatic carbonate preparation process using 3 or 4 reactive distillation columns, one or more of the following features may be preferred:

1) First of all, it is preferred to introduce the top stream comprising dialkyl carbonate and alkyl alcohol from the first reactive distillation column into a fifth distillation column, and to recover from such fifth distillation column a top stream comprising alkyl alcohol and a bottom stream comprising dialkyl carbonate. Said bottom stream may be sent to the first reactive distillation column. A substream comprising alkyl alcohol may be split from said top stream and used to reactivate used catalyst in above-mentioned step (i). Preferably, said substream is combined with the bottom stream comprising diaryl carbonate and used catalyst from the fourth reactive distillation column, before any catalyst recycle.

2) Secondly, it is preferred to introduce the top stream comprising dialkyl carbonate and aryl alcohol from the second distillation column into a sixth distillation column, and to recover from such sixth distillation column a top stream comprising dialkyl carbonate and a bottom stream comprising aryl alcohol. Said top stream may be sent to the fifth distillation column. A substream comprising aryl alcohol may be split from said bottom stream and used to reactivate used catalyst in above-mentioned step (i). Preferably, said substream is combined with the bottom stream comprising

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diaryl carbonate and used catalyst from the fourth reactive distillation column, before any catalyst recycle.

3) Thirdly, it is preferred to send the top stream comprising aryl alcohol from the optional third reactive
5 distillation column to the second reactive distillation column, preferably by introducing it into the line by which the bottom stream from the first reactive distillation column is introduced into the second reactive distillation column.

Examples of the aromatic carbonate preparation process of
10 the present invention are shown in Figures 1 and 2. The set-ups as shown in Figures 1 and 2 may be used to produce diphenyl carbonate (DPC) from diethyl carbonate (DEC) and phenol in three reactive distillation columns 3, 9 and 18. However, these set-ups may also be used to prepare DPC from
15 any other dialkyl carbonate and phenol or to prepare any other diaryl carbonate from a dialkyl carbonate and an aryl alcohol.

In Figures 1 and 2, DEC is continuously passed via line 1 into first reactive distillation column 3. Via line 2 phenol
20 is also continuously fed into first reactive distillation column 3. Further, via line 2 fresh homogeneous catalyst is added, which catalyst may for example be $\text{Ti}(\text{OEt})_4$ dissolved in ethanol or DEC.

A mixture comprising DEC, ethanol and phenol is withdrawn
25 from first reactive distillation column 3 via line 4. Said mixture is passed to distillation column 5 where it is separated into a top fraction comprising ethanol and DEC that is withdrawn via line 6 and a bottom fraction comprising DEC and phenol that is recycled to first reactive distillation
30 column 3 via line 7.

A mixture comprising catalyst, phenol, DEC, ethyl phenyl carbonate (EPC) and DPC is withdrawn from first reactive distillation column 3 via line 8. Said mixture is then passed

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to second reactive distillation column 9 where it is separated into a top fraction and a bottom fraction. The top fraction comprises DEC, phenol and ethanol and is sent to distillation column 12 via line 11. The bottom fraction
5 comprises catalyst, DPC, EPC and phenol and is sent to third reactive distillation column 18 via line 10.

In distillation column 12, a separation takes place into a top fraction comprising DEC and ethanol and a bottom fraction comprising phenol. The top fraction is sent to
10 distillation column 5 via line 13. The bottom fraction is sent to first reactive distillation column 3 via lines 14 and 2 consecutively.

In third reactive distillation column 18, a separation takes place into a top fraction comprising phenol and EPC and
15 withdrawn via line 20 and a bottom fraction comprising catalyst and DPC and withdrawn via line 19. Said top fraction is recycled to second reactive distillation column 9 via lines 20 and 8 consecutively. Said bottom fraction is sent to a fourth reactive distillation column 21.

20 In fourth reactive distillation column 21, a separation takes place into a top fraction comprising DPC and withdrawn via line 22, so as to recover DPC before below-described catalyst reactivation, and a bottom fraction comprising used catalyst and DPC and withdrawn via line 23.

25 In Figure 1, the bottom fraction comprising used catalyst and DPC from fourth reactive distillation column 21 is recycled to first reactive distillation column 3 via lines 23, 29 and 2 consecutively. Optionally, a part of said bottom fraction may be bled from the process via line 30.

30 In the set-up of Figure 1, the used catalyst in the bottom fraction from fourth reactive distillation column 21 may be regenerated in multiple ways, some of which are shown in Figure 1. Firstly, the catalyst may be contacted with

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fresh phenol or recycle phenol. Catalyst reactivation may take place through the addition of fresh phenol via line 2 to which the catalyst in line 29 is sent. Further, the catalyst may be contacted with fresh phenol by adding fresh phenol via line 24 to line 29. Catalyst reactivation may also take place through the addition of recycle phenol via line 14 to line 2 to which the catalyst in line 29 is sent. Further, the catalyst may be contacted with recycle phenol by splitting part of the recycle phenol containing stream in line 14 and sending that to line 29 via line 25. Secondly, the catalyst may be contacted with fresh ethanol or recovered ethanol. Catalyst reactivation may take place through the addition of fresh ethanol via line 27 to line 2 to which the catalyst in line 29 is sent. Further, the catalyst may be contacted with fresh ethanol by adding fresh ethanol via line 24 to line 29. Further, the catalyst may be contacted with recovered ethanol by splitting part of the recovered ethanol containing stream in line 6 and sending that via lines 31 and 28 to line 2 to which the catalyst in line 29 is sent, or sending that via lines 31 and 26 to line 29.

In Figure 2, the bottom fraction comprising used catalyst and DPC from fourth reactive distillation column 21 is recycled to second reactive distillation column 9 via lines 23, 29 and 8 consecutively. Optionally, a part of said bottom fraction may be bled from the process via line 30.

In the set-up of Figure 2, the used catalyst in the bottom fraction from fourth reactive distillation column 21 may be regenerated in multiple ways, some of which are shown in Figure 2. Catalyst reactivation may take place through contacting the used catalyst in line 8 with unconverted phenol coming from first reactive distillation column 3, to which line 8 the used catalyst in line 29 is sent. Further, the catalyst may be contacted with fresh phenol or recycle

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phenol. The catalyst may be contacted with fresh phenol by adding fresh phenol via line 24 to line 29 or by adding fresh phenol via line 32 to line 8 to which the catalyst in line 29 is sent. Still further, the catalyst may be contacted with
5 recycle phenol by splitting part of the recycle phenol containing stream in line 14 and sending that via lines 31 and 27 to line 8 to which the catalyst in line 29 is sent, or sending that via lines 31 and 25 to line 29. Finally, the catalyst may be contacted with fresh ethanol or recovered
10 ethanol. The catalyst may be contacted with fresh ethanol by adding fresh ethanol via line 24 to line 29 or by adding fresh ethanol via line 32 to line 8 to which the catalyst in line 29 is sent. Further, the catalyst may be contacted with recovered ethanol by splitting part of the recovered ethanol
15 containing stream in line 6 and sending that via lines 33 and 28 to line 8 to which the catalyst in line 29 is sent, or sending that via lines 33 and 26 to line 29.

In the set-ups of Figures 1 and 2, only the used catalyst from the bottom fraction from fourth reactive distillation
20 column 21 is regenerated. However, it is envisaged by the present inventors that used catalyst from any one of the bottom fractions from reactive distillation columns 3, 9 and 18 may be partially or completely subjected to the catalyst reactivation process of the present invention in similar
25 ways. Further, catalyst reactivation in accordance with the the present invention can be carried out in similar ways in a case where only 1, 2 or 3 reactive distillation column(s), instead of 4, is or are used.

Still further, the present invention relates to a process
30 for making a polycarbonate from a diaryl carbonate prepared in accordance with the aromatic carbonate preparation process of the present invention. Accordingly, the present invention relates to a process for making a polycarbonate, comprising

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reacting a dihydroxy aromatic compound with a diaryl carbonate prepared in accordance with the above-described aromatic carbonate preparation process. Further, accordingly, the present invention relates to a process for making a polycarbonate, comprising preparing a diaryl carbonate in accordance with the above-described aromatic carbonate preparation process, and reacting a dihydroxy aromatic compound with the diaryl carbonate thus obtained. The embodiments and preferences as described above with reference to the aromatic carbonate preparation process of the present invention also apply to said diaryl carbonate preparation step of the polycarbonate make process of the present invention.

Further, preferably, said dihydroxy aromatic compound is bisphenol A, which is 4,4'-(propan-2-ylidene)diphenol. The production of polycarbonate by the polymerisation of diaryl carbonate with an aromatic dihydroxy compound, such as bisphenol A, is well known. See for example US5747609, WO2005026235 and WO2009010486, the disclosures of which are herein incorporated by reference.

The invention is further illustrated by the following Examples.

Examples

In the Examples, a used catalyst was reactivated by applying the catalyst reactivation process of the present invention.

Before said reactivation, the used catalyst had been used in a process for preparing an aromatic carbonate, wherein diphenyl carbonate (DPC) was prepared from diethyl carbonate (DEC) and phenol, in the presence of a homogeneous catalyst which was added to the process as $\text{Ti}(\text{OEt})_4$ dissolved in ethanol. The set-up used to prepare said DPC is schematically shown in Figures 1 and 2. Reactivation in accordance with the

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present invention was applied to the used catalyst as contained in the stream in line 23 coming from fourth reactive distillation column 21. Said stream contained a mixture which comprised 68 wt.% of DPC, 1 wt.% of EPC and 31 wt.% of the used, titanium-containing catalyst (10% of which catalyst was the metal titanium, which is 3.1 wt.% based on total mixture, the remainder being the ligands). The molar ratio of the carbonates (DPC and EPC) to titanium in said mixture was 5:1.

10 The activity of reactivated catalyst in the following two reactions was measured:

Reaction 1 (Table 1 below): $2\text{EPC} \rightarrow \text{DPC} + \text{DEC}$

Reaction 2 (Table 2 below): $\text{DEC} + \text{PhOH} \rightarrow \text{EPC} + \text{EtOH}$

wherein: EPC = ethyl phenyl carbonate; DPC = diphenyl carbonate; DEC = diethyl carbonate; PhOH = phenol; and EtOH = ethanol.

In order to reactivate the used catalyst, it was mixed with phenol and heated at 180 °C for 15 minutes. In the reactivation for reaction 1, the PhOH:Ti molar ratio was either 45:1 or 10:1. In the reactivation for reaction 2, the PhOH:Ti molar ratio was 391:1. In the latter case, phenol was not only used to reactivate the catalyst but was also used as a reactant in subsequent reaction 2. Therefore, a relatively high amount of phenol was used in the reactivation step, and no additional phenol was added in reaction 2.

In all of the experiments comprising a reactivation step, the resulting reactivated catalyst containing solution in phenol was not purified but used as such in the next reaction step (reaction 1 or 2).

30 The activity of reactivated catalyst in reactions 1 and 2 was measured. In the activity measurement experiments, the catalyst and reactant(s) were mixed and heated at 180 °C. Samples from the resulting mixture were taken at the start

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and after 15, 30 and 60 minutes and analyzed by gas chromatography (GC). The GC results were used to calculate the EPC conversion (Table 1) or the phenol conversion (Table 2).

Table 1: Catalyst activity for the 2EPC → DPC + DEC reaction

Catalyst	Starting composition (at 180 °C)			EPC conversion (%)		
	EPC (g)	Catalyst ⁽²⁾ (g)	Ti (ppmw)	15 min.	30 min.	60 min.
Fresh Ti(OPh) ₄	5.021	0.049	1090	7.00	16.20	31.20
Not-reactivated	5.032	0.181	1087	0.07	0.11	2.74
A: Reactivated ⁽¹⁾	5.002	0.192	1050	6.84	14.83	26.10
B: Reactivated ⁽¹⁾	5.194	0.186	1060	1.43	3.68	18.24

⁽¹⁾ In the reactivation step, the used catalyst was mixed with phenol at a PhOH:Ti ratio of 45:1 (case A) or 10:1 (case B). Further, in the reactivation step, the molar ratio of phenol to carbonates [DPC + EPC] was 6.2:1 (case A) and 1.4:1 (case B).

⁽²⁾ The amounts shown here refer either to (i) pure (fresh) catalyst Ti(OPh)₄, or (ii) amount of the solution containing used catalyst dissolved in carbonates (the solution having the following, above-mentioned composition (and obtained in the way as described above): 31 wt.% of the used titanium-containing catalyst, 68 wt.% of DPC and 1 wt.% of EPC) before said catalyst was reactivated by mixing with phenol.

Table 2: Catalyst activity for the DEC + PhOH → EPC + EtOH reaction

Catalyst	Starting composition (at 180 °C)				PhOH conversion (%)		
	DEC (g)	PhOH (g)	Catalyst ⁽²⁾ (g)	Ti (ppmw)	15 min.	30 min.	60 min.
Fresh Ti (OPh) ₄	2.511	2.500	0.029	655	5.00	9.69	12.44
Reactivated ⁽¹⁾	2.494	2.554	0.106	644	4.75	9.31	12.02

⁽¹⁾ In the reactivation step, the used catalyst was mixed with phenol at a PhOH:Ti ratio of 391:1. Further, in the reactivation step, the molar ratio of phenol to carbonates [DPC + EPC] was 55:1.

⁽²⁾ See note (2) under Table 1.

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As can be seen in Tables 1 and 2, the catalyst reactivation process of the present invention advantageously resulted in a substantial restoration of the activity of the used catalyst to its original level, that is to say the activity of fresh catalyst. In relation to the 2EPC $\rightarrow$ DPC + DEC reaction (Table 1), catalyst activity (EPC conversion at 60 minutes) was restored from 9% (used, not-reactivated catalyst) to 58% at a PhOH:Ti ratio of 10:1 or even 84% at a PhOH:Ti ratio of 45:1. Further, in relation to the DEC + PhOH $\rightarrow$ EPC + EtOH reaction (Table 2), catalyst activity (PhOH conversion at 60 minutes) of the reactivated catalyst was also significantly increased, namely to 97% of the activity of fresh catalyst.

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C L A I M S

1. Process for reactivating a used catalyst, wherein:

the used catalyst is a homogeneous catalyst comprising titanium, tin or lead and one or more ligands, which has been used in a process for preparing an aromatic carbonate which comprises reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate; and

the used catalyst is contacted with an aryl alcohol or an alkyl alcohol in the presence of one or more carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate, wherein the aryl group in the aryl alcohol with which the used catalyst may be contacted is identical to the aryl group in the alkyl aryl carbonate or aryl alcohol used as reactant in said process for preparing an aromatic carbonate; wherein the alkyl group in the alkyl alcohol with which the used catalyst may be contacted is identical to the alkyl group in the dialkyl carbonate or alkyl aryl carbonate used as reactant in said process for preparing an aromatic carbonate; and wherein the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is at least 0.5:1, suitably at least 1:1.

2. Process for preparing an aromatic carbonate, comprising:

reacting a dialkyl carbonate or an alkyl aryl carbonate with an aryl alcohol or an alkyl aryl carbonate in the presence of a homogeneous catalyst comprising titanium, tin or lead and one or more ligands, resulting in an aromatic carbonate which is an alkyl aryl carbonate or a diaryl carbonate; and

contacting the catalyst used in said reaction step with an aryl alcohol or an alkyl alcohol in the presence of one or

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more carbonates selected from the group consisting of dialkyl carbonate, alkyl aryl carbonate and diaryl carbonate, wherein the aryl group in the aryl alcohol with which the used catalyst may be contacted is identical to the aryl group in the alkyl aryl carbonate or aryl alcohol used as reactant in said reaction step; wherein the alkyl group in the alkyl alcohol with which the used catalyst may be contacted is identical to the alkyl group in the dialkyl carbonate or alkyl aryl carbonate used as reactant in said reaction step; and wherein the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is at least 0.5:1, suitably at least 1:1.

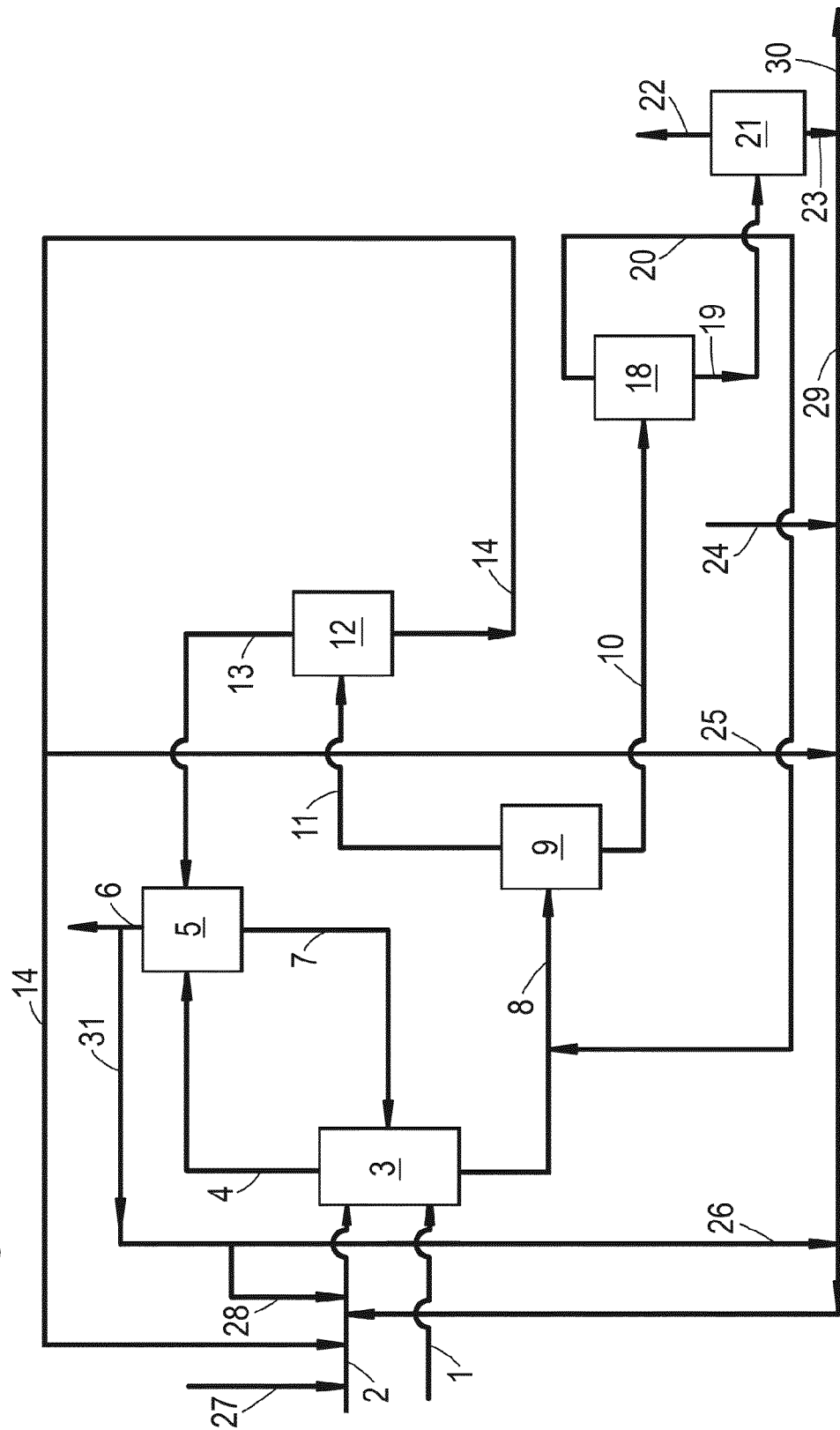
3. Process according to claim 1 or 2, wherein the molar ratio of the aryl alcohol or alkyl alcohol to the carbonates is of from 0.5:1 to 3.7:1.

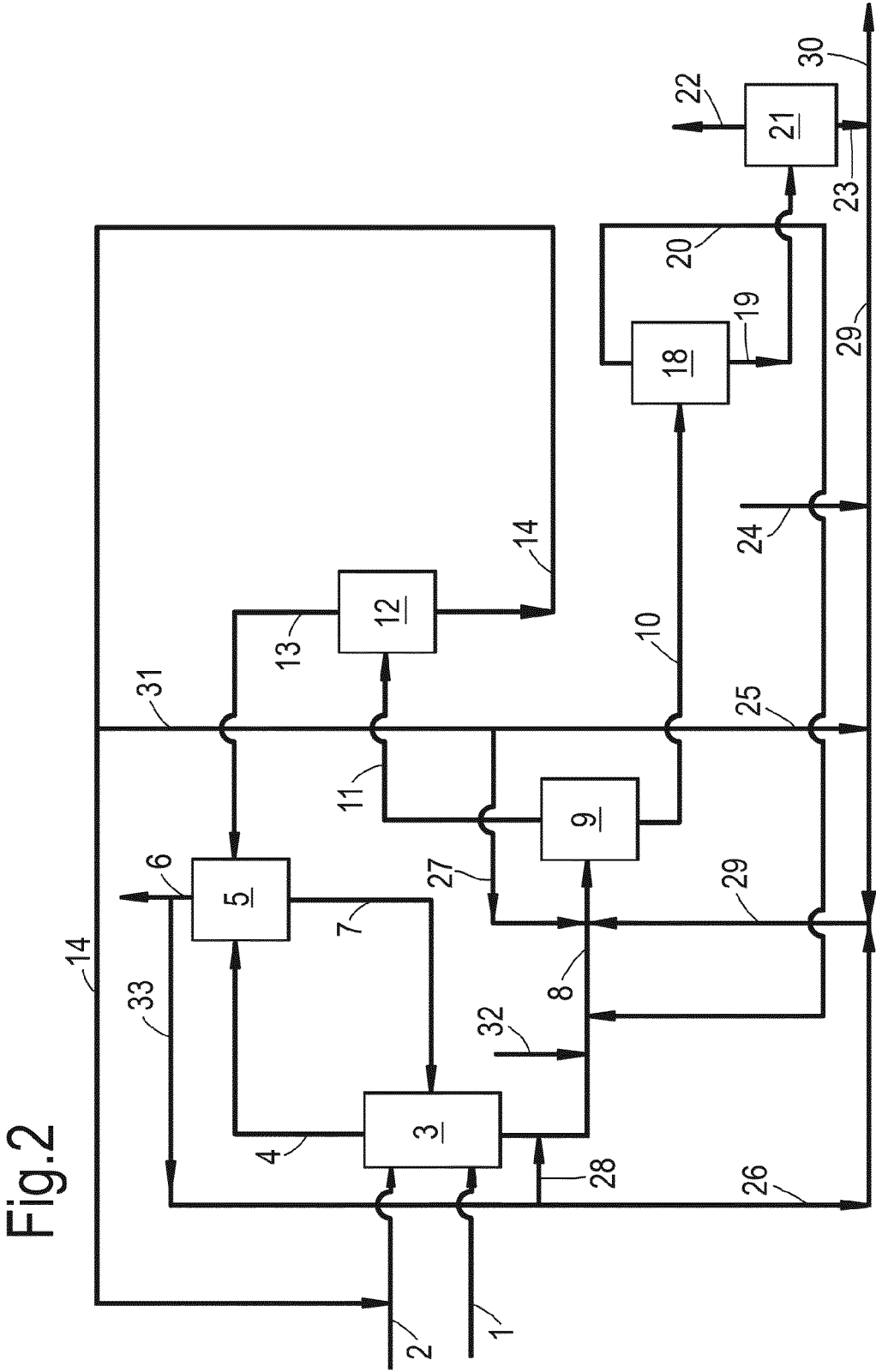
4. Process according to any one of the preceding claims, wherein the time period for contacting the used catalyst with the aryl alcohol or alkyl alcohol is of from 1 second to 10 days.

5. Process according to any one of the preceding claims, wherein the temperature during contacting the used catalyst with the aryl alcohol or alkyl alcohol is of from 100 to 400 °C.

6. Process for making a polycarbonate, comprising preparing a diaryl carbonate in accordance with the process of any one of claims 2-5, and reacting a dihydroxy aromatic compound with the diaryl carbonate thus obtained.

Fig. 1





INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/081702

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C68/06 C07C69/96 C08G64/30 B01J38/52
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)

C07C C08G B01J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 1 016 648 A1 (ASAHI CHEMICAL IND [JP]) 5 July 2000 (2000-07-05) cited in the application page 47, paragraph 190; figure 5 -----	1,2,4-6
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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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

1 March 2017

Date of mailing of the international search report

08/03/2017

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/081702

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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INTERNATIONAL SEARCH REPORT

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