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(54) **Title:** BIFUNCTIONAL CATALYST

(57) **Abstract:** A bifunctional catalyst for conversion of oxygenates, said catalyst comprising zeolite, alumina binder and Zn, wherein the Zn is present at least partly as ZnAl₂O₄.



WO 2017/093335 A1

Title: Bifunctional catalyst

Conversion of methanol to hydrocarbons over zeolite catalysts has been known for decades, and several variations of the process have been commercialized including
5 MTG (methanol-to-gasoline), MTO (methanol-to-olefins), and MTP (methanol-to-propylene). In order to produce a physically robust catalyst, it is necessary to use a binder material. This binder is usually an oxide such as alumina, silica, magnesia etc.

A catalyst may be optimized to emphasize various functions such as product yield or
10 selectivity. However, when one function is optimized the resulting catalyst will often show less advantageous with respect to other parameters. An example may be a catalyst optimized to achieve a higher product yield but which then shows a decreased selectivity. Thus, a special task in developing new catalyst is to improve the catalyst on
15 essential parameters without adverse effect to other important features.

In a first aspect of the present invention is provided a catalyst which enables an improved aromatics yield

In a second aspect of the present is provided a catalyst which enables a reduced
20 MeOH cracking to non-desired products such as CO and CO₂.

In a third aspect of the present invention is provided a catalyst which substantially regains activity after regeneration.

25 These and other advantages are achieved by a bifunctional catalyst for example for conversion of oxygenates and dehydrogenation of hydrocarbons, said catalyst comprising zeolite, alumina binder and Zn, wherein the Zn is present at least partly as ZnAl₂O₄.

To increase the yield of aromatics, a bifunctional catalyst containing acidic zeolite sites
30 as well as dehydrogenation sites e.g. metal or oxide is provided. This means that a stream comprising one or more oxygenates e.g. methanol may be converted in the presence of the catalyst into hydrocarbons rich in aromatics while dehydrogenation of hydrocarbons such as naphthenes, paraffins and/or isoparaffins, into olefins and/or aromatics also takes place.

In preferred embodiments the catalyst is optimized for conversion of oxygenates such as methanol and/or DME into aromatics (herein abbreviated MTA).

- 5 The binder may be a pure alumina binder or an alumina-based binder further comprising mixtures of aluminum oxide and aluminum hydroxide and/or e.g. silica/alumina.

10 The zeolite may for example be one of the commonly known zeolites used in MTA and MTG processes. For example H-ZSM-5 may be a preferred zeolite for the present catalyst due to its unique pore structure leading to favorable size selectivity as well as its relatively low coking rate. H-ZSM-5 may be particularly preferred in case of MTA processes.

15 Examples of Zn/ZSM-5 catalysts with low content of Zn such as 1 wt% Zn for MTA are known and it has been argued that higher Zn content is to be avoided in order to avoid methanol cracking to carbon oxides. However, the applicant has shown that a high Zn content in the catalyst may result in an improved aromatics yield in MTA processes compared to known catalysts. Thus, in several advantageous embodiments the total Zn content in the catalyst is 3 – 25 wt%, 5 – 20 wt%, 7 – 15 wt% or 8 – 13 wt%, such as
20 more than 7 wt% Zn, more than 10 wt% Zn or 12 wt% or more Zn.

25 Depending on the production process the Zn in the catalyst may be present in various concentrations in both binder and zeolite of the present catalyst. E.g. in some embodiments the Zn concentration is higher in the binder phase than in the zeolite phase which for example may be the case where the Zn is applied by impregnation.

30 A catalyst wherein Zn is present in both zeolite and alumina binder allows for industrial production by “simple” means such as by impregnation. For example, a bifunctional catalyst as herein described may be achieved by Zn impregnation of a “base catalyst” comprising an alumina binder and a zeolite such as ZSM-5. A preferred base catalyst comprises 30-50 % binder and 50-70 % zeolite.

The impregnation may be carried out by contacting the zeolite or the zeolite and alumina binder with a Zn-containing solution. The solution may preferably be aqueous, but

other solvents than water may be preferred as well. Impregnation may also be carried out by contacting the zeolite or the zeolite and alumina binder with a solid Zn compound, e.g., by mixing and/or grinding or other treatments to ensure intimate mixing of the components.

5

The Zn source may be any Zn-containing, organic and/or inorganic, compound. Preferred compounds comprise zinc nitrate, zinc acetate and zinc oxide, hydroxide, carbonate or mixtures hereof.

10

In order to provide a functional catalyst the impregnation will typically be followed by calcination or similar treatment(s).

15

However, when a zeolite or an alumina/zeolite based catalyst is impregnated with Zn in order to obtain the desired amount of Zn in the zeolite, significant amounts of Zn may also be introduced into the binder, for example, as ZnO and/or ZnAl_2O_4 . Various ratios of ZnO/ ZnAl_2O_4 may be achieved depending on the treatment of the impregnated catalyst.

20

The applicant has shown that in a desirable catalyst Zn in the alumina binder is present mainly as ZnAl_2O_4 . Defining the relative amount of zinc oxide, ZnO, in the binder phase as molar percentage of Zn present as ZnO relative to the total amount of Zn contained in the binder phase it may be desirable to have a catalyst where the amount of ZnO present in the binder phase is less than 50%, or preferably less than 10%, such as less than 5% or less than 2%, preferably less than 1%, such as 0.5% or less than 0.1% ZnO.

25

I.e. it may be preferred that the Zn in the binder has been fully spinelized, according to the reaction equation $\text{ZnO} + \text{Al}_2\text{O}_3 \rightarrow \text{ZnAl}_2\text{O}_4$, meaning that all or substantially all of the Zn in the binder is present as ZnAl_2O_4 .

30

Preferably a large part of the Zn in the alumina binder is present as ZnAl_2O_4 . Defining the relative amount of ZnAl_2O_4 in the binder phase as molar percentage of Zn present as ZnAl_2O_4 relative to the total amount of Zn contained in the binder phase, in some embodiments 50 – 100% of the Zn in the binder is present as ZnAl_2O_4 , for example

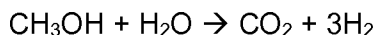
more than 60%, more than 70% or more than 80%. In some advantageous embodiments 85 – 100% of the Zn in the binder is present as ZnAl_2O_4 , such as more than 90% or more than 95%.

5 As shown by the applicant cracking of MeOH may be avoided with a high degree of spinelization, it may be preferred especially in case of high Zn content in the catalyst that more than 97% of the Zn in the binder is present as ZnAl_2O_4 , such as more than 98%, more than 99%, more than 99,5% or more than 99,8% of the Zn in the binder is present as ZnAl_2O_4 . Optimal and practically achievable ZnAl_2O_4 content ranges may be
10 95 – 100% in the binder is present as ZnAl_2O_4 , such as 97% - 99,9% Zn in the binder is present as ZnAl_2O_4 .

In preferred embodiments the catalyst has been fully spinelized meaning that all or substantially all of the Zn in the binder is present as ZnAl_2O_4 .

15 ZnO in the binder is active in cracking methanol which is an undesired reaction in MTA. Depending on the means of production and after-treatment of the catalyst more or less of the Zn in the alumina binder may be present as ZnAl_2O_4 . Steaming or calcination of a Zn impregnated catalyst as commonly applied in production of metal/zeolite systems
20 may result in a partial spinelization of the Zn ($\text{ZnO} + \text{Al}_2\text{O}_3 \rightarrow \text{ZnAl}_2\text{O}_4$). However, it has been shown that with a high Zn content even a relatively high degree of spinelization may lead to substantial MeOH cracking, but that a very desirable catalyst is achieved with a high degree of or preferably full spinelization of Zn in the alumina binder i.e. where all or substantially all of Zn in the binder is present as ZnAl_2O_4 .

25 A bifunctional catalyst where all of or substantially all Zn in the binder is present as ZnAl_2O_4 and where substantially no ZnO is present in the binder as described herein exhibits a low selectivity to CO_x even if the Zn content is high e.g. above 9 wt%. Thus, in preferred embodiments the fresh (start of run) catalyst has a CO_x selectivity (determined at 420°C, 20 bar, 10 mol% methanol and a WHSV of 1.6) below 8 % preferably
30 below 7 % such as 6% or below, or 5% or lower, or even 2% or lower. The CO_x selectivity is defined as the molar percentage of methanol in the feed converted into CO and CO_2 according to the net reactions:



5 Thus, by the present application is provided a preferred bifunctional catalyst comprising alumina binder, H- ZSM-5 and 8 – 15 wt% Zn in the total catalyst and where the Zn in the binder is fully or substantially fully spinelized. Said catalyst provides a high aromatics yield in a MTA reaction while cracking of the methanol is reduced to below 7%.

10 An exemplary bifunctional catalyst may desirably comprise 30-65 wt% H-ZSM-5, 5-40 wt% ZnAl_2O_4 , 0-40 wt% Al_2O_3 , 0-10 wt% ZnO.

The catalyst may further in some embodiments be characterized by having 0.1-12 wt% such as 1 - 7 wt% Zn present in the zeolite phase.

15

Alternatively it may comprise 50-60 wt% H-ZSM-5, 10-35 wt% ZnAl_2O_4 , 2-25 wt% Al_2O_3 , 0-7 wt% ZnO. In order to avoid the presence of free ZnO in the binder phase, it may be beneficial to have at least a small excess of Al_2O_3 which is not spinelized in reaction with ZnO. Using a higher amount of Al_2O_3 in the preparation of the "base catalyst" will lead to a more robust catalyst preparation process.

20

Due to gradual coking of the catalyst during operation the catalyst must be regenerated at intervals in a stream comprising O_2 .

25 A partially spinelized catalyst with a moderate to high ZnAl_2O_4 :ZnO ratio may e.g. be obtained by heating the Zn-impregnated base catalyst at 300-500°C in air.

30 A partially spinelized catalyst with a very high ZnAl_2O_4 :ZnO content, fully spinelized catalyst or a substantially fully spinelized catalyst may be obtained by heating the Zn impregnated catalyst at 300 – 550°C in steam or in an atmosphere comprising at least 10 vol%, 30 vol% 50 vol% or 80 vol% steam.

A partially spinelized catalyst with a very high ZnAl_2O_4 :ZnO content, fully spinelized

catalyst or a substantially fully spinelized catalyst may be obtained by heating a partially spinelized catalyst at 300 – 550°C in steam or in an atmosphere comprising at least 10 vol%, 30 vol% 50 vol% or 80 vol% steam.

- 5 An at least partially spinelized catalyst, preferably a partially spinelized catalyst with a very high ZnAl_2O_4 content, fully spinelized catalyst or a substantially fully spinelized catalyst as described herein may be provided in numerous ways including obtaining a desired spinelized catalyst during production or by producing a catalyst with a spinelization degree below the desired spinelization percentage and followed by steaming said catalyst in a subsequent step e.g. as in an in situ steaming step to obtain a catalyst with a desired degree of spinelization.

10 Various methods may be applied to produce the bifunctional catalyst: The two components (Zn and Zeolite) may constitute an integrated entity, e.g. as obtained by introducing the Zn component by impregnation or ion-exchange to the zeolite, either onto the zeolite itself or onto an extrudate in which the zeolite is embedded in an alumina binder. The Zn component may also be added in the form of a salt, either as a solid or in solution, or an oxide, hydroxide or carbonate together with the zeolite, binder and/or lubricants prior to shaping, e.g. during extrusion or pelletization.

20 The post-impregnation treatment (calcination or similar heat treatment) is preferably carried out in a humid atmosphere, e.g., by heating the Zn impregnated base catalyst at 300 – 550°C in steam or in an atmosphere comprising at least 10 vol%, 30 vol% 50 vol% or 80 vol% steam.

25 Also physical mixtures of several acidic and metal components may be applied and the mixture may be charged to the reactor to form a uniform mixture or to form alternating layers or they may be graded to various degrees.

- 30 Thus, there is provided a method for producing a bifunctional catalyst comprising an alumina binder, zeolite and Zn, said method comprising the steps of
- impregnating an alumina/zeolite catalyst with a Zn-containing aqueous solution
 - at least partly spinelizing the Zn impregnated alumina/zeolite catalyst by heating the impregnated alumina/zeolite catalyst to 300 – 650°C for 0.25 – 7 h.

- method for producing a bifunctional catalyst comprising an alumina binder, zeolite and Zn, said method comprising the steps of
- impregnating/applying a Zn compound or a solution of a Zn compound onto a zeolite or alumina/zeolite by mixing
- shaping said mixture by extrusion or pelletization
- at least partly spinelizing the Zn impregnated alumina/zeolite catalyst by heating the impregnated alumina/zeolite catalyst to 300 – 650°C for 0.25 – 7 h.

10 **Example 1: Preparation of catalyst**

A base catalyst containing 65 wt % H-ZSM-5 and 35% Al₂O₃ was prepared by mixing followed by extrusion following well known procedures. Upon calcination, samples of the base catalyst were impregnated with an aqueous solution containing zinc nitrate at different Zn concentrations. The resulting pore-filled extrudates were heated to 470°C in air and kept at 470°C for 1 h to obtain catalysts with various amounts of Zn.

Example 2: Catalyst activity and regeneration

20 Catalysts prepared by the procedure described in example 1 were subjected to conversion of methanol at 420°C in an isothermal fixed bed reactor. N₂ was used as an inert co-feed to obtain a methanol concentration of 7 mol% in the reactor inlet. The total pressure was 20 bar, and the space velocity (WHSV) of methanol was 2 h⁻¹.

25 Zn/H-ZSM-5 catalysts suffer from reversible as well as irreversible deactivation. Deposition of carbon (coke) on the catalyst is responsible for reversible deactivation. In the example shown in table 1, the deactivated (coked) catalyst is regenerated by removal of the deposited carbon by combustion in a flow of 2% O₂ (in N₂) at 500°C.

30 Due to irreversible deactivation, the catalyst did not fully regain its activity after regeneration. The results in table 1 show, that a catalyst containing 10% Zn is able to regain significantly more of its original activity after regeneration than a catalyst containing 5% Zn.

Table 1: Catalyst activity after regeneration. Wt% of aromatics in hydrocarbon product is defined as the mass of aromatics relative to the total mass of hydrocarbons in the effluent stream.

Zn content (wt%)	Aromatics in total hydrocarbon product (wt%)	Percentage of aromatics selectivity regained after regeneration
5	52	90
10	51	95

Example 3: Stability towards steaming

To simulate catalyst activity after extended operation under industrial conditions, the catalysts were subjected to methanol conversion after steaming under severe conditions. Methanol conversion was performed under the same conditions as in example 2. The results in Table 2 show that the catalyst containing 10% Zn retains significantly more of its original activity than the catalyst containing 5 wt% Zn after severe steaming.

Table 2: Loss of catalyst activity upon severe steaming (100% steam for 48h at 500°C and 1 bar). Wt% of aromatics in hydrocarbon product is defined as the mass of aromatics relative to the total mass of hydrocarbons in effluent stream.

Zn content (wt%)	Aromatics in hydrocarbon product (wt%), fresh catalyst	Aromatics (wt%) in hydrocarbon product, steamed catalyst
5	52	28
10	51	36

Example 4: Methanol cracking vs. Zn content

Cracking (decomposition) of methanol/DME can occur via several mechanisms. For example the acidic sites in the catalyst may catalyze cracking of DME to CH₄, CO, and

H₂, while certain Zn species catalyze cracking of methanol to CO and H₂. CO₂ can be formed as a primary cracking product or indirectly via the water gas shift reaction.

When methanol is converted over a catalyst containing Zn, part of the methanol is converted to CO_x due to cracking, which results in lower yield of hydrocarbon products.

Methanol conversion has been performed at 420°C, 20 bar, 10mol% methanol (N₂ balance), and a space velocity (WHSV) of 1.6.

The results in Table 3 were obtained using catalysts prepared according to example 1.

The results show that the cracking activity is highly dependent on the amount of Zn, i.e. higher Zn content leads to higher cracking activity.

Table 3: CO_x selectivity at different contents of Zn

Zn content (wt%)	CO _x selectivity (%)
0	<0.1
3	2
5	4
10	9

Example 5: CO_x selectivity after calcination and steaming

A base catalyst containing 65% ZSM-5 and 35% Al₂O₃ was impregnated with aqueous zinc nitrate solution. The resulting pore filled extrudates were calcined in air and steam, respectively. Furthermore, the catalyst calcined in air was subjected to steaming after calcination. Methanol conversion over these catalysts was performed using the same conditions as in example 4.

The results in table 4 show that the presence of steam during calcination of the impregnated catalyst or heating the catalyst in the presence of steam after calcination leads to lower selectivity to CO_x. This observation may be rationalized by the fact that the presence of steam leads to formation of ZnAl₂O₄ rather than free ZnO in the binder phase.

Table 4: CO_x selectivity for catalysts containing 10% Zn, calcined in the presence of different amounts of steam

Condition	CO _x selectivity (%)
Calcined in air	9
Calcined in steam (500°C, 2h)	2
Calcined in air, steamed after calcination (500°C, 5 h)	4
Calcined in air, steamed after calcination (500°C, 48 h)	<0.1

Claims

1. A bifunctional catalyst comprising zeolite, alumina binder and Zn, wherein the Zn is present at least partly as ZnAl_2O_4 .
5
2. Bifunctional catalyst according to claim 1, where the bifunctional catalyst is a catalyst for conversion of oxygenates.
3. Bifunctional catalyst according to claim 1 or 2 wherein the zeolite is ZSM-5 or ZSM-11.
10
4. Bifunctional catalyst according to any of the preceding claims, wherein the catalyst is an extruded or pelletized catalyst.
5. Bifunctional catalyst according to any of the preceding claims comprising 30-80 wt% zeolite, 5-40 wt% ZnAl_2O_4 , 0-40 wt% Al_2O_3 , 0-10 wt% ZnO.
15
6. Bifunctional catalyst according to any of the preceding claims wherein Zn is present in both zeolite and alumina binder.
20
7. Bifunctional catalyst according to any of the preceding claims wherein the alumina binder further comprises silica.
8. Bifunctional catalyst according to any of the preceding claims wherein the catalyst, by X-ray diffraction, does not contain free ZnO in the binder.
25
9. Bifunctional catalyst according to any of the preceding claims wherein the Zn concentration is 3-25 wt%, such as 7 – 15wt% such as 8 – 12wt% in the catalyst.
10. Bifunctional catalyst according to any of the preceding claims wherein Zn is present in the binder as mainly ZnAl_2O_4 .
30
11. Bifunctional catalyst according to any of the preceding claims wherein the amount of Zn present in the binder phase as ZnAl_2O_4 corresponds to at least 50% ZnAl_2O_4 , at

least 60%, at least 70%, at least 80%, or at least 90% ZnAl_2O_4 relative to the total amount of Zn in the binder phase.

5 12. Bifunctional catalyst according to any of the preceding claims wherein the amount of Zn present in the binder phase as ZnAl_2O_4 corresponds to at least 95% ZnAl_2O_4 , such as at least 96%, at least 98%, at least 99%, at least 99,3%, at least 99,5%, at least 99,8% or 100% ZnAl_2O_4 , relative to the total amount of Zn present in the binder phase.

10 13. Bifunctional catalyst according to any of the preceding claims wherein the amount of Zn present in the binder phase as ZnO corresponds to up to 10% ZnO, Such as less than 5% ZnO or less than 2% ZnO, preferably less than 1% ZnO, such as 0,5% ZnO or less than 0.1% ZnO.

15 14. Bifunctional catalyst according to any of the preceding claims wherein Zn in the zeolite is present as ZnO, $\text{Zn}(\text{OH})^+$ and/or Zn^{++} in ion exchange positions.

20 15. Bifunctional catalyst according to any of the preceding claims wherein the total Zn content in the catalyst is 3 – 25 wt%, 8 – 15wt% or 9 – 13 wt%, such as more than 7wt% Zn, more than 10 wt% Zn or 12 or more wt% Zn.

16. Bifunctional catalyst according to any of the preceding claims wherein said catalyst is partly or fully spinelized.

25 17. Bifunctional catalyst according to any of the preceding claims wherein the Zn content is substantially the same in its partly spinelized and fully spinelized form.

30 18. Bifunctional catalyst according to any of the preceding claims wherein a fully spinelized form is obtained by heating a partly spinelized form at 300 – 550°C in an atmosphere comprising steam.

19. A bifunctional catalyst according to any of the preceding claims, used in an oxygenate conversion process comprising:

- a conversion step wherein a feed stream comprising oxygenates such as methanol and/or DME is converted into a hydrocarbon stream rich in aromatics in presence of said bifunctional catalyst.

5 20. A bifunctional catalyst according to any of the preceding claims, wherein the oxygenate conversion process comprises:

- a separation step wherein the hydrocarbon stream rich in aromatics is separated into at least an aromatics rich product stream, a stream comprising water and a recycle stream.

10

21. Method for producing a bifunctional catalyst comprising an alumina binder, zeolite and Zn, said method comprising the steps of

- impregnating an alumina/zeolite catalyst with a Zn-containing aqueous solution
- at least partly spinelizing the Zn impregnated alumina/zeolite catalyst by heating the

15

impregnated alumina/zeolite catalyst to 300 – 650°C for 0.25 – 7 h.

22. Method for producing a bifunctional catalyst comprising an alumina binder, zeolite and Zn, said method comprising the steps of

- impregnating a Zn compound or a solution of a Zn compound onto a zeolite or alumina/zeolite by mixing
- shaping said mixture by extrusion or pelletization
- at least partly spinelizing the Zn impregnated alumina/zeolite catalyst by heating the

20

impregnated alumina/zeolite catalyst to 300 – 650°C for 0.25 – 7 h.

25 23. Method according to claim 21 or 22 wherein the zeolite is a ZSM preferably H-ZSM-5.

24. Method according to claim 21 - 23 wherein the Zn aqueous solution is a Zn nitrate solution or a Zn acetate solution.

30

25. Method according to claim any of the claims 21 – 24, wherein Zn impregnation and calcination and/or spinelization results in a total Zn content of 3 – 25 wt%, 8 – 15wt% or 9 – 13 wt%, such more than 7wt% Zn, more than 10 wt% Zn or 12 or more wt% Zn.

26. Method according to any of the claims 21 - 25 wherein the Zn concentration is higher in the binder phase than in the zeolite phase.

5 27. Method according to any of the preceding claims 21 - 26 wherein the catalyst is further or fully spinelized by heating a partly spinelized form at 300 – 550°C in an atmosphere comprising steam

28. A catalyst and method according to claim 1 - 27, where the selectivity to aromatics is 30-80%, as determined at 420°C, 20 bar, 10 mol% methanol and a WHSV of 1.6.

10

29. A catalyst and method according to claim 1 - 28, where the selectivity to CO_x is 0-10% as determined at 420°C, 20 bar, 10 mol% methanol and a WHSV of 1.6.

15

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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ADD.

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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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.
X	US 6 156 689 A (KIMBLE JAMES B [US] ET AL) 5 December 2000 (2000-12-05) column 1, line 8 - line 13 column 1, line 19 - line 37 column 1, line 53 - column 2, line 38 column 3, line 1 - line 9 column 3, line 31 - line 41 column 4, line 4 - line 48 column 5, line 64 - column 6, line 4 column 7, line 9 - line 54 column 8, line 3 - line 17 catalyst AA; column 10, line 44 - line 49 catalyst EE; column 10, line 66 - column 11, line 34 catalyst N; column 14, line 46 - line 54 column 15, line 58 - column 16, line 8 table IV claims 1, 8, 9, 12, 15, 16, 20, 22-24	1-29



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.

INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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