(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 December 2015 (30.12.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/197585 A1

(51) **International Patent Classification**:
B01J 23/08 (2006.01) ***B01J 23/00*** (2006.01)
B01J 37/04 (2006.01) ***C07C 2/00*** (2006.01)
B01J 37/03 (2006.01) ***C07C 13/00*** (2006.01)
B01J 37/06 (2006.01) ***C07C 15/00*** (2006.01)
B01J 37/08 (2006.01)

(21) **International Application Number**:
PCT/EP2015/064049

(22) **International Filing Date**:
23 June 2015 (23.06.2015)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
14173671.0 24 June 2014 (24.06.2014) EP

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2015/197585 A1

(54) **Title**: NOVEL METHYLATION CATALYSTS

(57) **Abstract**: The present invention is directed to methylation catalysts comprising gallium oxide, which preferably further contain magnesium oxide. In a preferred embodiment of the present invention, the methylation catalyst consists of gallium oxide and magnesium oxide. The present invention is further directed to the use of such catalysts for the methylation of phenol and its methylated derivatives having one or two methyl groups such as o-cresol, m-cresol, p-cresol, 2,3-xylenol, 2,4-xylenol, 2,5-xylenol, 2,6-xylenol and 3,5-xylenol.

Novel methylation catalysts

The present invention is directed to methylation catalysts comprising gallium oxide, which preferably further contain magnesium oxide. In a preferred embodiment of the present invention, the methylation catalyst consists of gallium oxide and magnesium oxide. The term "consisting of" in the context of the present invention means that the total amount of gallium oxide and magnesium oxide ideally sums up to 100 weight-%. It is, however, not excluded that small amounts of impurities (such as e.g. any other metal) or non-reactive additives may be present in amounts of less than 5 weight-%, preferably less than 1 weight-%, more preferably less than 0.5 weight-%, based on the total weight of the methylation catalyst. The present invention is further directed to the use of such catalysts for the methylation of phenol and its methylated derivatives having one or two methyl groups such as o-cresol, m-cresol, p-cresol, 2,3-xylenol, 2,4-xylenol, 2,5-xylenol, 2,6-xylenol and 3,5-xylenol.

The invention is now described in more detail below.

Methylation catalyst

In an embodiment of the present invention the methylation catalyst comprises gallium oxide.

In a preferred embodiment of this embodiment the methylation catalyst further comprises magnesium oxide. Thus, the present invention is also directed to a methylation catalyst comprising gallium oxide and magnesium oxide. The term "gallium oxide and magnesium oxide" also encompasses mixed oxides of gallium and magnesium, as well as any mixture of Ga_2O_3 and MgO, and mixtures of any modifications thereof. These (mixed) oxides of gallium and magnesium do not have a spinel structure.

In a further embodiment of the present invention the methylation catalyst consists of gallium oxide. The term “consisting of” in the context of the present invention means that the total amount of gallium oxide ideally is 100 weight-%. It is, however, not excluded that small amounts of impurities (such as e.g. any other metal) or non-reactive additives may be present in amounts of less than 5 weight-%, preferably less than 1 weight-%, more preferably less than 0.5 weight-%, based on the total weight of the methylation catalyst.

In another embodiment of the present invention the methylation catalyst consists of gallium oxide and magnesium oxide. Hereby also mixed oxides of gallium and magnesium are encompassed, as well as any mixture of Ga_2O_3 and MgO, and mixtures of any modifications thereof. The term “consisting of” in the context of the present invention means that the total amount of gallium oxide and magnesium oxide ideally sums up to 100 weight-%. It is, however, not excluded that small amounts of impurities (such as e.g. any other metal) or non-reactive additives may be present in amounts of less than 5 weight-%, preferably less than 1 weight-%, more preferably less than 0.5 weight-%, based on the total weight of the methylation catalyst.

In preferred embodiments of the methylation catalysts either comprising gallium oxide/s and magnesium oxide/s or consisting of gallium oxide/s and magnesium oxide/s the weight-ratio of magnesium to gallium is in the range of from 1:1 to 15:1. Especially preferred are those methylation catalysts where the weight-ratio of magnesium to gallium is either 2 : 1 or 6 : 1 or 10 : 1.

In a preferred embodiment of the present invention the methylation catalyst with all preferences and limitations as given above does not contain iron oxide in contrast to the catalysts disclosed in EP-A 019 476.

In a further preferred embodiment of the present invention the methylation catalyst consisting of gallium oxide with all preferences and limitations as given above does neither contain titanium oxide nor indium oxide in contrast to US 5,245,089 and US 3,418,379, respectively.

Process for the manufacture of the methylation catalysts

Usually the catalysts are prepared as follows:

a) dissolving gallium nitrate and optionally magnesium nitrate in the desired ratio in water;

b) providing a sodium carbonate solution with a concentration in the range of 0.3 to 2 M (preferably with a concentration in the range of 0.8 to 1.5 M) and a pH value in the range of 7.5 to 10 (preferably a pH value in the range of 8 to 9), whereby the molar ratio of sodium carbonate to the sum of gallium nitrate and optionally magnesium nitrate is 5 : 1;

c) dropping the solution obtained in step a) into the solution obtained in step b) under stirring, while adjusting the pH to a value in the range of 6 to 8 (preferably to a value in the range of 6.5 to 7.5) and keeping the temperature in the range of 50 to 60°C;

d) filtering the solution obtained in step c) to obtain the solid methylation catalyst;

e) washing the solid methylation catalyst obtained in step d) with water;

f) drying the solid methylation catalyst obtained in step e);

g) calcinating the dried solid methylation catalyst obtained in step f) in air.

The steps are now described in more detail below.

Step a)

This step is usually performed at room temperature, but may be also performed at temperatures above room temperature. It is only important that the salts, i.e. gallium nitrate and optionally magnesium nitrate, become dissolved. The pressure at which this step is performed is not critical. It is also possible to use other magnesium or gallium salts such as magnesium halogenides or gallium halogenides as long as the salts are removed by the calcination step g).

Step b)

If needed the pH value is adjusted by means of concentrated HNO_3. Other acids may also be suitable, if other salts of Ga and Mg are used. Thus, it is e.g. possible to use concentrated hydrogen chloride if Ga chloride and Mg chloride are used.

Step c)

The pH is preferably adjusted with concentrated sodium hydroxide. Other bases such as other alkaline bases and earth alkaline bases may also be suitable as long as the formed salts are better soluble than MgO and Ga_2O_3. Stirring is continued for about 30 to 45 minutes.

Step d)

For filtering any suitable filter such as a Büchner filter may be used.

Step e)

The washing with water is preferably continued until the elution water shows a pH value of 7.

Step f)

The drying may be carried out at a temperature in the range of from 100 to 150°C for 4 to 48 hours. In one embodiment of the process of the present invention the drying is carried out at 120°C for 4 hours, in another embodiment of the process of the present invention the drying is carried out at 110°C for 12 hours.

Step g)

The calcination is preferably carried out at a temperature in the range of from 400 to 600°C, for a time in the range of 4 to 15 hours.
More preferably the calcination is carried out at 450°C for 8 hours.

Use of the methylation catalysts

The present invention is also directed to the use of the methylation catalysts as described above for the methylation of a compound selected from the group consisting of phenol and its methylated derivatives having one or two methyl groups.

Examples of methylated phenol derivatives with one methyl group are ortho-cresol (o-cresol), meta-cresol (m-cresol) and para-cresol (p-cresol).

Examples of methylated phenol derivatives with two methyl groups are 2,3-xylenol, 2,4-xylenol, 2,5-xylenol, 2,6-xylenol and 3,5-xylenol.

Preferred examples of methylation reactions which may be catalyzed by the methylation catalysts according to the present invention as described above are:
Methylation of phenol to o-cresol (see examples 1-3),
methylation of phenol to 2,6-xylenol (see examples 4-8),

methylation of phenol to 2,4,6-trimethylphenol (see examples 9-12),
methylation of o-cresol to 2,6-xylenol (see examples 13-22),
methylation of o-cresol to 2,4,6-trimethylphenol (see examples 23-25), and
methylation of 2,6-xylenol to 2,4,6-trimethylphenol (see examples 26-32).

Thus, preferred starting materials are phenol, o-cresol and 2,6-xylenol.

Further examples of methylation reactions which may be catalyzed by the methylation catalysts according to the present invention as described above are:
Methylation of m-cresol to 2,5-xylenol (the reaction conditions are similar to the methylation of o-cresol to 2,6-xylenol),
methylation of m-cresol to 2,3-xylenol (the reaction conditions are similar to the methylation of o-cresol to 2,6-xylenol),
methylation of m-cresol to 2,3,6-trimethylphenol (the reaction conditions are similar to the methylation of o-cresol to 2,4,6-trimethylphenol),
methylation of p-cresol to 2,4-xylenol (the reaction conditions are similar to the methylation of o-cresol to 2,6-xylenol),
methylation of p-cresol to 2,4,6-trimethylphenol (the reaction conditions are similar to the methylation of o-cresol to 2,4,6-trimethylphenol),
methylation of 2,3-xylenol to 2,3,6-trimethylphenol (the reaction conditions are similar to the methylation of o-cresol to 2,6-xylenol),
methylation of 2,4-xylenol to 2,4,6-trimethylphenol (the reaction conditions are similar to the methylation of o-cresol to 2,6-xylenol),
methylation of 2,5-xylenol to 2,3,6-trimethylphenol (the reaction conditions are similar to the methylation of m-cresol to 2,3-xylenol),
methylation of 3,5-xylenol to 2,3,5-trimethylphenol (the reaction conditions are similar to the methylation of m-cresol to 2,3-xylenol),
methylation of 3,5-xylenol to 2,3,5,6-tetramethylphenol (the reaction conditions are similar to the methylation of phenol to 2,6-xylenol).

The single methylation reactions are now described in more detail below. The GHSV (gas hourly space velocity) is thereby in the range of from 3200 h^{-1} to 4000 h^{-1}, more preferably the GHSV is around 3600 h^{-1}.

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Methylation of phenol to o-cresol

The preferred methylation catalyst has a molar magnesium to gallium ratio in the range of from 0 : 1 to 10 : 1, more preferably the molar magnesium to gallium ratio is 0 : 1.

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The preferred temperature is in the range of from 350 to 450°C, preferably the temperature is around 400°C. Preferably the pressure is in the range of from 1 to 10 bara (bar absolute), more preferably it is 1 bara.

15 The molar ratio of methanol to water to phenol is (2 to 5) : (0 to 5) : 1, preferably the molar ratio is 10 : 0 : 1.

Methylation of phenol to 2,6-xylenol

20 The preferred methylation catalyst has a molar magnesium to gallium ratio in the range of from 0 : 1 to 10 : 1, more preferably the molar magnesium to gallium ratio is 0 : 1.

The preferred temperature is in the range of from 350 to 500°C, preferably the
25 temperature is in the range of 400 to 450°C. Preferably the pressure is in the range of from 1 to 10 bara (bar absolute), more preferably it is 1 bara.

The molar ratio of methanol to water to phenol is (3 to 15) : (0 to 5) : 1, preferably the molar ratio is 10 : 0 : 1.

Methylation of phenol to 2,4,6-trimethylphenol

The preferred methylation catalyst has a molar magnesium to gallium ratio in the range of from 2 : 1 to 10 : 1, more preferably the molar magnesium to gallium ratio is 10 : 1.

The preferred temperature is in the range of from 350 to 500°C, preferably the temperature is around 450°C. Preferably the pressure is in the range of from 1 to 10 bara (bar absolute), more preferably it is 1 bara.

The molar ratio of methanol to water to phenol is (4 to 15) : (0 to 5) : 1, preferably the molar ratio is 5 : 0 : 1.

Methylation of o-cresol to 2,6-xylenol

The preferred methylation catalyst has a molar magnesium to gallium ratio in the range of from 0 : 1 to 10 : 1, more preferably the molar magnesium to gallium ratio is 0 : 1.

The preferred temperature is in the range of from 300 to 450°C, preferably the temperature is in the range of from 350 to 400°C. Preferably the pressure is in the range of from 1 to 10 bara (bar absolute), more preferably it is 1 bara.

The molar ratio of methanol to water to o-cresol is (2 to 15) : (0 to 7) : 1, preferably the molar ratio is 5 : 0 : 1.

Methylation of o-cresol to 2,4,6-trimethylphenol

The preferred methylation catalyst has a molar magnesium to gallium ratio in the range of from 2 : 1 to 6 : 1, more preferably the molar magnesium to gallium ratio is 2 : 1.

The preferred temperature is in the range of from 300 to 400°C, preferably the temperature is around 350°C. Preferably the pressure is in the range of from 1 to 10 bara (bar absolute), more preferably it is 1 bara.

The molar ratio of methanol to water to o-cresol is (3 to 15) : (0 to 5) : 1, preferably the molar ratio is 5 : 5 : 1.

Methylation of 2,6-xylenol to 2,4,6-trimethylphenol

The preferred methylation catalyst has a molar magnesium to gallium ratio in the range of from 2 : 1 to 10 : 1, more preferably the molar magnesium to gallium ratio is 10 : 1.

The preferred temperature is in the range of from 350 to 450°C, preferably the temperature is around 400°C. Preferably the pressure is in the range of from 1 to 10 bara (bar absolute), more preferably it is 1 bara.

The molar ratio of methanol to water to 2,6-xylenol is (2 to 15) : (0 to 5) : 1, preferably the molar ratio is 5 : 5 : 1.

The invention is now further illustrated in the following non-limiting examples.

Examples

All examples have been carried out according to the general procedure.

General procedure

In a typical experiment, 1 cm^3 of catalyst is loaded in the reactor, with particles having a size in the range of from 30 to 60 mesh, prepared by compressing the powder into particles, then crushed and sieved. The liquid mixture is then prepared, with the desired methanol/phenolic compound molar ratio, loaded in the syringe and installed on the pump. The gas flow rate is then set up and regulated (typically N_2), with a flow rate that is typically equal to 20 mL/min (when the reaction temperature is 400°C). The temperature of the reactor is then raised, and when the needed temperature is reached, the reaction time is started. Typical conditions are: 1 second of contact time (GHSV 3600 h^{-1}), calculated on the basis of the overall gas/vapour flow. The overall content of organics in the inlet flow (phenol + methanol) is between 15 and 18 volume%; it may change within this interval because the N_2 flow is changed in function of the reaction temperature used. Moreover, if also water is fed, by means of a second syringe and pump, the N_2 flow is decreased proportionally, so to keep the overall flow of inert (after vaporisation of water) constant. The amount of organic fed (and vaporised) is typically 0.46 mL/h.

During the experiment, the outlet flow is made bubbling in a isopropanol solution, and the compounds which cannot be condensed are then sent to the vent. After 50 minutes of reaction time, the syringe is stopped, and the N_2 is let flow for some minutes more. The isopropanol solution is transferred in a vessel, brought to 25 mL volume with isopropanol, then 20 microL of standard are added (n-decane), and then the mixture is analysed by GC (Thermo Instrumento, capillary column HP5, FID detector).

Examples 1-3: Methylation of phenol to o-cresol

Example 1: Use of Ga_2O_3 as catalyst

Selectivity = 86%

Conversion = 38%

Catalyst: Ga_2O_3

Feed: Phenol/Methanol (1:10) (molar ratio)

T = 400°C

Example 2: Use of Ga_2O_3 as catalyst

Selectivity: 66%

Conversion: 59%

Feed: MeOH/Phenol = 10 : 1 (molar ratio)

Temperature: 400°C

Example 3: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 54%

Conversion: 9%

Feed: MeOH/water/Phenol = 10 : 5 : 1 (molar ratio)

Temperature: 400°C

Examples 4-8: Methylation of phenol to 2,6-xylenol

Example 4: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 89%

Conversion: 99%

Feed: MeOH/Phenol = 10 : 1 (molar ratio)

Temperature: 500°C

Example 5: Use of Ga_2O_3 as catalyst

Selectivity: 64%

Conversion: 96%

Feed: MeOH/Phenol = 10 : 1 (molar ratio)

Temperature: 400°C

Example 6: Use of Ga_2O_3 as catalyst

Selectivity: 64%

Conversion: 90%

Feed: MeOH/Phenol = 10 : 1 (molar ratio)

Temperature: 450°C

Example 7: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 60%

Conversion: 91%

Feed: MeOH/Phenol = 10 : 1 (molar ratio)

Temperature: 400°C

Example 8: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 59%

Conversion: 89%

Feed: MeOH/Phenol = 10 : 1 (molar ratio)

Temperature: 400°C

Examples 9-12: Methylation of phenol to 2,4,6-trimethylphenol

Example 9: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 79%

Conversion: 100%

Feed: MeOH/Phenol = 5 : 1 (molar ratio)

Temperature: 450°C

Example 10: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 62%

Conversion: 100%

Feed: MeOH/water/Phenol = 10 : 5 : 1 (molar ratio)

Temperature: 410°C

Example 11: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 66%

Conversion: 100%

Feed: MeOH/Phenol = 10 : 1 (molar ratio)

Temperature: 450°C

Example 12: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 45%

Conversion: 100%

Feed: MeOH/water/Phenol = 10 : 5 : 1 (molar ratio)

Temperature: 400°C

Examples 13-22: Methylation of o-cresol to 2,6-xylenol

Example 13: Use of Ga_2O_3 as catalyst

Selectivity: 93%

Conversion: 18%

Feed: o-cresol/MeOH = 1 : 5 (molar ratio)

Temperature: 350°C

Example 14: Use of Ga_2O_3 as catalyst

Selectivity: 91%

Conversion: 37%

Feed: o-cresol/MeOH = 1 : 5 (molar ratio)

Temperature: 350°C

Example 15: Use of Ga_2O_3 as catalyst

Selectivity: 89%

Conversion: 25%

Feed: o-cresol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 350°C

Example 16: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 92%

Conversion: 37%

Feed: o-cresol/MeOH = 1 : 5 (molar ratio)

Temperature: 350°C

Example 17: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 77%

Conversion: 67%

Feed: o-cresol/MeOH = 1 : 5 (molar ratio)

Temperature: 350°C

Example 18: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 69%

Conversion: 60%

Feed: o-cresol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 350°C

Example 19: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 67%

Conversion: 100%

Feed: o-cresol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 400°C

Example 20: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 6 to 1

Selectivity: 83%

Conversion: 45%

Feed: o-cresol/MeOH = 1 : 5 (molar ratio)

Temperature: 350°C

Example 21: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 6 to 1

Selectivity: 63%

Conversion: 49%

Feed: o-cresol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 350°C

Example 22: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 86%

Conversion: 37%

Feed: o-cresol/MeOH = 1 : 5 (molar ratio)

Temperature: 350°C

Examples 23-25: Methylation of o-cresol to 2,4,6-trimethylphenol

Example 23: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 58%

Conversion: 76%

Feed: o-cresol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 350°C

Example 24: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 54%

Conversion: 76%

Feed: o-cresol/MeOH = 1 : 5 (molar ratio)

Temperature: 350°C

Example 25: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 6 to 1

Selectivity: 46%

Conversion: 53%

Feed: o-cresol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 350°C

Examples 26-32: Methylation of 2,6-xylenol to 2,4,6-trimethylphenol

Example 26: Use of Ga_2O_3 as catalyst

Selectivity: 66%

Conversion: 8%

Feed: 2,6-xylenol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 400°C

Example 27: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 2 to 1

Selectivity: 78%

Conversion: 51%

Feed: 2,6-xylenol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 400°C

Example 28: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 6 to 1

Selectivity: 69%

Conversion: 42%

Feed: 2,6-xylenol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 400°C

Example 29: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 96%

Conversion: 74%

Feed: 2,6-xylenol/water/MeOH = 1 : 5 : 5 (molar ratio)

Temperature: 400°C

Example 30: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 84%

Conversion: 38%

Feed: 2,6-xylenol/MeOH = 1 : 5 (molar ratio)

Temperature: 400°C

Example 31: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 93%

Conversion: 28%

Feed: 2,6-xylenol/MeOH = 1 : 2.5 (molar ratio)

Temperature: 400°C

Example 32: Use of a Mg-Ga-oxide-catalyst with a weight ratio of Mg to Ga of 10 to 1

Selectivity: 94%

Conversion: 52%

Feed: 2,6-xylenol/water/MeOH = 1 : 2.5 : 2.5 (molar ratio)

Temperature: 400°C

Example 33: Preparation of the catalysts

25.8 g of $Mg(NO_3)_2$ are dissolved in 110 mL of water, together with an amount of Ga in the form of $Ga(NO_3)_3$ necessary to obtain the desired Mg/Ga ratio. For example, for the catalyst with Mg/Ga 10/1, the amount of Ga salt is 2.57 g. Separately, 3.14 g of Na_2CO_3 are dissolved in water, to prepare 20 ml of a second solution 1 M, and containing an overall amount of Na_2CO_3 which corresponds to a number of moles 5 times the number of Ga+Mg moles. The pH of this latter solution is eventually adjusted to the value of 8.5 by means of concentrated HNO3. Then the first solution is dropped into the second one, while keeping the

pH at 8.5 and the temperature at 50-60°C; the pH is adjusted with concentrated NaOH. Then the solution is left under stirring for 30-45 min. The slurry is then filtered with a buchner, and the solid is then washed with abundant water until the elution water shows a pH about 7. The solid is then dried at 120°C for 4 h or at 110°C overnight. Then the dried solid is calcined in air for 8h at 450°C, in order to decompose the precursor and form the Mg/Ga mixed oxide.

Claims

1. A methylation catalyst comprising gallium oxide.

2. The methylation catalyst according to claim 1 further comprising magnesium oxide.

3. The methylation catalyst according to claim 2 comprising mixed gallium and magnesium oxides.

4. The methylation catalyst according to claim 1 consisting of gallium oxide.

5. The methylation catalyst according to claim 4 neither containing titanium oxide nor indium oxide.

6. The methylation catalyst according to claim 2 or 3 consisting of gallium oxides and magnesium oxides.

7. The methylation catalyst according to claim 2, 3 or 6, whereby the weight-ratio of magnesium to gallium is in the range of from 1:1 to 15:1.

8. The methylation catalyst according to any one or more of the preceding claims, wherein the methylation catalyst does not contain iron oxide(s).

9. The methylation catalyst according to any one or more of the preceding claims, wherein the methylation catalyst is for the methylation of phenol and its methylated derivatives having one or two methyl groups, preferably wherein the methylation catalyst is for the methylation of phenol, o-cresol, m-cresol, p-cresol, 2,3-xylenol, 2,4-xylenol, 2,5-xylenol, 2,6-xylenol and 3,5-xylenol, more

preferably wherein the methylation catalyst is for the methylation of phenol, o-cresol and 2,6-xylenol.

10. Use of the catalyst according to any one or more of the preceding claims for the methylation of a compound selected from the group consisting of phenol and its methylated derivatives having one or two methyl groups.

11. The use according to claim 10, wherein the methylated derivative of phenol having one or two methyl groups is selected from the group consisting of o-cresol, m-cresol, p-cresol, 2,3-xylenol, 2,4-xylenol, 2,5-xylenol, 2,6-xylenol and 3,5-xylenol.

12. The use according to claim 10, wherein the compound is selected from the group consisting of phenol, o-cresol and 2,6-xylenol.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/064049

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/08 B01J37/04 B01J37/03 B01J37/06 B01J37/08
B01J23/00 C07C2/00 C07C13/00 C07C15/00
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)
B01J C07C

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 5 245 089 A (IRICK JR GETHER [US] ET AL) 14 September 1993 (1993-09-14) abstract column 2, line 67 - column 3, line 2 examples 1,7	1,8
X	EP 0 019 476 A2 (MITSUI PETROCHEMICAL IND [JP]) 26 November 1980 (1980-11-26) abstract claim 1 examples 10,16,17 tables 2,3	1-12
X	US 3 418 379 A (PARSEY EDWARD S ET AL) 24 December 1968 (1968-12-24) abstract column 1, lines 9-11,48-57	1,4,5,8

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 September 2015	17/09/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Fischbach, Malaika

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CAPLUS, [Online] 1 January 2001 (2001-01-01), CHOUDHARY VASANT R ET AL: "Friedel - Crafts type alkylation of benzene and other aromatic compounds using MgGa2O4 (spinel)-MgO based catalysts", XP002526851, retrieved from CAPLUS Database accession no. 2002-100380 abstract page 332, right-hand column, lines 1-6 -----	1-3,6-9
X	CHOI ET AL: "Balancing acidity and basicity for highly selective and stable modified MgO catalysts in the alkylation of phenol with methanol", CATALYSIS TODAY , 63(2-4), 229-236 CODEN: CATTEA; ISSN: 0920-5861,, 1 January 2000 (2000-01-01), XP002743429, DOI: 10.1016/S0920-5861(00)00464-8 10.1016/S0920-5861(00)00464-8 abstract table 1 -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/064049

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5245089 A	14-09-1993	NONE	
EP 0019476 A2	26-11-1980	DE 3066141 D1	23-02-1984
		EP 0019476 A2	26-11-1980
		US 4329517 A	11-05-1982
US 3418379 A	24-12-1968	NONE	