



(51) International Patent Classification:

B01J 29/74 (2006.01)

C07C 2/74 (2006.01)

B01J 29/12 (2006.01)

C07C 5/367 (2006.01)

B01J 29/03 (2006.01)

(21) International Application Number:

PCT/US2019/028503

(22) International Filing Date:

22 April 2019 (22.04.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/666,330

03 May 2018 (03.05.2018)

US

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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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, 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,

(54) Title: PREPARATION OF AN HYDROALKYLATION CATALYST

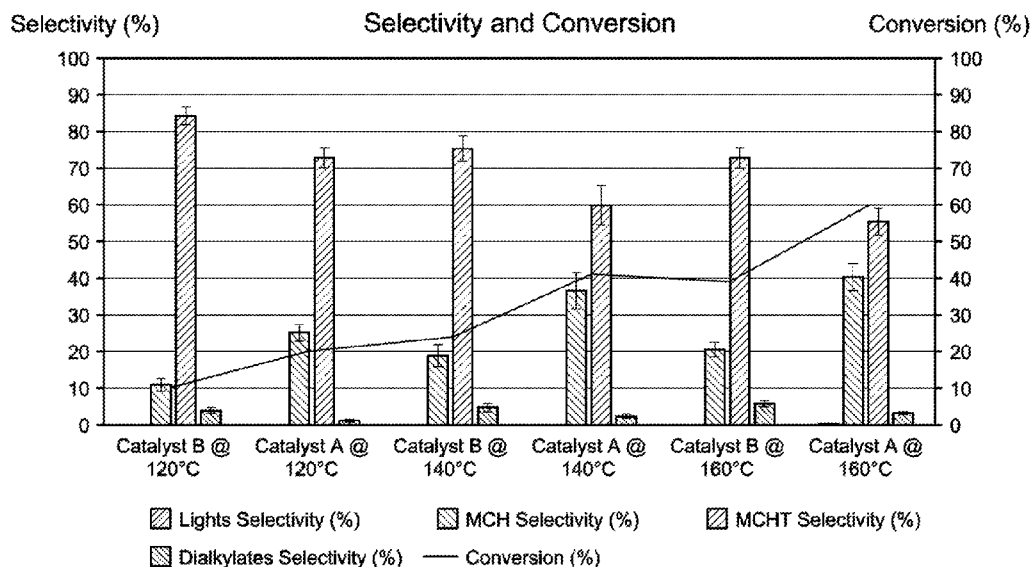


FIG. 1

(57) Abstract: A process for preparing a hydroalkylation catalyst comprising providing a hydroalkylation catalyst precursor comprising an acidic component and a hydrogenation component; and treating the catalyst precursor in the presence of water vapor at a temperature ranging from 200°C to 600°C to obtain the hydroalkylation catalyst.



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).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

PREPARATION OF AN HYDROALKYLATION CATALYST

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5 **[0001]** This application claims the benefit of U.S. Provisional Application No. 62/666,330, filed May 3, 2018, the disclosure of which is incorporated herein by reference.

FIELD

[0002] This disclosure relates to hydroalkylation catalysts, their preparation and their use in producing cycloalkylaromatic compounds.

10 **BACKGROUND**

[0003] Catalytic hydroalkylation of aromatic compounds, such as toluene and xylenes, to produce cycloalkylaromatic compounds, such as (methylcyclohexyl)toluenes and (dimethylcyclohexyl)xylenes, is an important reaction. For example, (methylcyclohexyl)toluenes can be dehydrogenated to produce methyl-substituted biphenyl
15 compounds, which can then be oxidized to produce biphenyl carboxylic acids. Biphenyl carboxylic acids are useful intermediates in the production of a variety of commercially valuable products, including polyesters and plasticizers for PVC and other polymer compositions.

[0004] One example of a process for the catalytic hydroalkylation of toluene and xylenes
20 and dehydrogenation of the resultant cycloalkylaromatic compounds to produce methyl-substituted biphenyl compounds is disclosed in US 2014/0275609, in which the hydroalkylation catalyst comprises an acidic component, such as a molecular sieve, and a hydrogenation component. Suitable molecular sieves are said to include BEA, FAU and MTW structure type materials, molecular sieves of the MCM-22 family, and mixtures thereof.
25 Suitable hydrogenation components are selected from the group consisting of palladium, ruthenium, nickel, zinc, tin, cobalt, and compounds and mixtures thereof. The exemplified catalysts are produced by impregnating the acidic component with an aqueous solution of the desired hydrogenation component. The impregnated sample is then dried and calcined in air. The entire contents of US 2014/0275609 are incorporated herein by reference.

30 **[0005]** One of the factors that influences the commercial viability of hydroalkylation/dehydrogenation as a route for the production of methyl-substituted biphenyl compounds, especially from toluene, is the yield of the 3,4'- and 4,4'-dimethylbiphenyl isomers since the 3,4' and 4,4' isomers are the most valuable intermediates in the manufacture of polyesters and plasticizers. An additional factor is the selectivity of the hydroalkylation

catalyst towards the desired monoalkylated product as distinct from dialkylated and other heavy species. There is therefore significant interest in developing hydroalkylation catalysts with the desired yield and selectivity profile.

SUMMARY

5 [0006] According to the present disclosure, it has now been found that controlled steaming of certain bifunctional hydroalkylation catalysts enhances the activity of the catalyst and decreases the selectivity toward dialkylated by-products in the catalytic hydroalkylation of aromatic compounds, such as toluene and xylenes, to produce cycloalkylaromatic compounds, such as (methylcyclohexyl)toluenes and (dimethylcyclohexyl)xylenes. While the reasons for
10 this advantageous result are not fully understood, it is believed that the steaming of the catalyst before reaction modifies the available surface acid sites, reducing the over-alkylation activity.

[0007] Thus, in one aspect, the disclosure provides a process for preparing a hydroalkylation catalyst, the process comprising:

(a) providing a hydroalkylation catalyst precursor comprising an acidic component
15 and a hydrogenation component; and

(b) treating the catalyst precursor in the presence of water vapor at a temperature ranging from 200°C to 600°C to obtain the hydroalkylation catalyst.

[0008] In further aspects, the present disclosure provides processes for producing cycloalkylaromatic compounds and methyl-substituted biphenyl compounds employing the
20 hydroalkylation catalyst described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Fig. 1 is a bar graph comparing the product selectivity for Catalysts A and B of Example 2 in the hydroalkylation of toluene at temperatures of 120, 140, and 160°C, a pressure of 10 bar, a weight hourly space velocity (WHSV) of 2, and a H₂:hydrocarbon molar ratio of
25 1.

[0010] Fig. 2 is a bar graph comparing the selectivity to 3,4'-, 4,3'- and 4,4'-isomers of (methylcyclohexyl)toluene (MCHT) for Catalysts A and B of Example 2 in the hydroalkylation of toluene at a temperatures of 120°C, 140°C, and 160 °C a pressure of 10 bar, a WHSV of 2, and a H₂:hydrocarbon molar ratio of 1.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0011] As used herein, "wt%" means percentage by weight, and "ppm wt" and "wppm" are used interchangeably to mean parts per million on a weight basis. All "ppm" as used herein are ppm by weight unless specified otherwise. All concentrations herein are expressed on the basis of the total amount of the composition in question. Thus, the concentrations of the various

components of the first mixture are expressed based on the total weight of the first mixture. All ranges expressed herein should include both end points as two specific embodiments unless specified or indicated to the contrary.

[0012] As used herein, "saturated air" refers to a gaseous mixture of air and water vapor where the partial pressure of the water vapor is equal to the saturation vapor pressure of water. It will be recognized for the purposes of this disclosure that saturation vapor pressure is a function of temperature.

[0013] Unless otherwise indicated, room temperature is 23°C.

[0014] Nomenclature of elements and groups thereof used herein are pursuant to the Periodic Table used by the International Union of Pure and Applied Chemistry after 1988. An example of the Periodic Table is shown in the inner page of the front cover of Advanced Inorganic Chemistry, 6th Edition, by F. Albert Cotton et al. (John Wiley & Sons, Inc., 1999).

[0015] The present disclosure relates to hydroalkylation catalysts which comprise an acidic component and a hydrogenation component and which have undergone treatment in the presence of water vapor at a temperature ranging from 200°C to 600°C. The present disclosure also relates to use of the resulting steamed catalysts in the hydroalkylation of toluene and/or xylenes to produce (methylcyclohexyl)toluenes (MCHT) and/or (dimethylcyclohexyl)xylenes, which can then be dehydrogenated to produce methyl-substituted biphenyl compounds. The steamed catalysts are found to exhibit improved activity and decreased dialkylate selectivity in the hydroalkylation of aromatic compounds, particularly toluene, than their non-steamed counterparts under the same hydroalkylation conditions.

Hydroalkylation Catalyst

[0016] The hydroalkylation catalyst employed herein is a bifunctional catalyst comprising a hydrogenation component and a solid acid alkylation component, typically a molecular sieve. The catalyst may also include a binder such as clay, silica, and/or a metal oxide. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be used as a binder include those of the montmorillonite and kaolin families, which families include the subbentonites and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment, or chemical modification. Suitable metal oxide binders include alumina, zirconia, titania, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, and silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-

alumina-zirconia, silica-alumina-magnesia, and silica-magnesia-zirconia.

[0017] Any known hydrogenation metal or compound thereof can be employed as the hydrogenation component of the catalyst. Examples of suitable metals include palladium, platinum, ruthenium, nickel, zinc, tin, and cobalt, with palladium being particularly advantageous. Preferably, the amount of hydrogenation metal present in the catalyst is between 0.05 and 10 wt %, such as between 0.1 and 5 wt %, of the catalyst.

[0018] Often, the solid acid alkylation component comprises a large pore molecular sieve having a Constraint Index (as defined in US 4,016,218) less than 2. Suitable large pore molecular sieves include zeolite beta, zeolite Y, Ultrastable Y (USY), Dealuminized Y (Deal Y), mordenite, ZSM-3, ZSM-4, ZSM-18, and ZSM-20. Zeolite ZSM-14 is described in US 3,923,636. Zeolite ZSM-20 is described in US 3,972,983. Zeolite Beta is described in US 3,308,069, and Re. No. 28,341. Low sodium Ultrastable Y molecular sieve (USY) is described in US 3,293,192 and US 3,449,070. Dealuminized Y zeolite (Deal Y) may be prepared by the method found in US 3,442,795. Zeolite UHP-Y is described in US 4,401,556. Mordenite is a naturally occurring material but is also available in synthetic forms, such as TEA-mordenite (i.e., synthetic mordenite prepared from a reaction mixture comprising a tetraethylammonium directing agent). TEA-mordenite is disclosed in US 3,766,093 and US 3,894,104. Preferred large pore molecular sieves comprise those selected from the group consisting of BEA, FAU, and MTW structure type molecular sieves, and mixtures and combinations thereof.

[0019] Alternatively, and more preferably, the solid acid alkylation component comprises a molecular sieve of the MCM-22 family, or a mixture or combination of a molecular sieve of the MCM-22 family and one of more of the large pore molecular sieves listed above. The term "MCM-22 family material" (or "material of the MCM-22 family" or "molecular sieve of the MCM-22 family"), as used herein, includes one or more of:

- molecular sieves made from a common first degree crystalline building block unit cell, which unit cell has the MWW framework topology. (A unit cell is a spatial arrangement of atoms which if tiled in three-dimensional space describes the crystal structure. Such crystal structures are discussed in the "Atlas of Zeolite Framework Types", Fifth edition, 2001, the entire content of which is incorporated as reference);

- molecular sieves made from a common second degree building block, being a 2-dimensional tiling of such MWW framework topology unit cells, forming a monolayer of one unit cell thickness, preferably one c-unit cell thickness;

- molecular sieves made from common second degree building blocks, being layers of one or more than one unit cell thickness, wherein the layer of more than one unit cell

thickness is made from stacking, packing, or binding at least two monolayers of one unit cell thickness. The stacking of such second degree building blocks can be in a regular fashion, an irregular fashion, a random fashion, or any combination thereof; and

- molecular sieves made by any regular or random 2-dimensional or 3-dimensional combination of unit cells having the MWW framework topology.

[0020] Molecular sieves of the MCM-22 family generally have an X-ray diffraction pattern including d-spacing maxima at 12.4 ± 0.25 , 6.9 ± 0.15 , 3.57 ± 0.07 and 3.42 ± 0.07 Angstrom. The X-ray diffraction data used to characterize the material are obtained by standard techniques using the K-alpha doublet of copper as the incident radiation and a diffractometer equipped with a scintillation counter and associated computer as the collection system. Molecular sieves of the MCM-22 family include MCM-22 (described in US 4,954,325), PSH-3 (described in US 4,439,409), SSZ-25 (described in US 4,826,667), ERB-1 (described in European Patent No. 0293032), ITQ-1 (described in US 6,077,498), ITQ-2 (described in International Patent Publication No. WO97/17290), MCM-36 (described in US 5,250,277), MCM-49 (described in US 5,236,575), MCM-56 (described in US 5,362,697), and mixtures and combinations thereof.

[0021] The hydrogenation component may be combined with the acidic component of the catalyst or the binder, if present, or the acidic component/binder composite by any known method, for example by impregnation or ion exchange with a solution of a salt of the desired metal. Thus, preferably, the acidic component can be mixed with the binder and a diluent, such as water, to form an extrudable paste. The paste can then be extruded into pellets of the required shape which, after drying and, if desired, calcination, can undergo impregnation or ion exchange with a solution of the desired metal salt. In some cases, an initial ammonium exchange and calcination may precede the metal addition so as to convert the acidic component to the active hydrogen form.

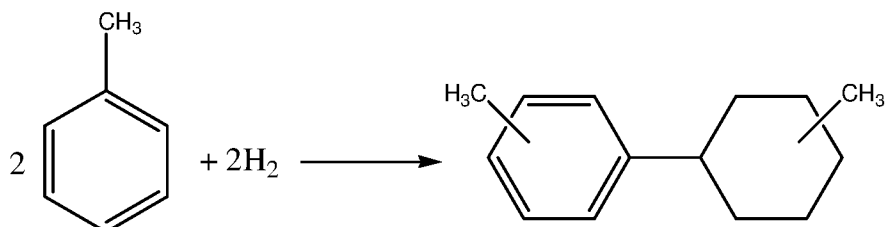
[0022] In accordance with the present disclosure, the hydroalkylation catalyst precursor produced by combining the acidic component and the hydrogenation component is steam treated before use in the presence of water vapor at a temperature ranging from 200°C to 600°C, such as from 250°C to 530°C, or from 300°C to 500°C, such as 510°C, to obtain the final hydroalkylation catalyst. Typically, the steam treatment is conducted at a pressure from 0.1 atm to 20 atm (10.1 kPa-a to 2027 kPa-a), preferably from 1 atm to 10 atm (101 kPa-a to 1013 kPa-a). Typically, the water vapor is supplied to the catalyst precursor in a gaseous stream, preferably a gaseous mixture of air and water vapor. Particularly preferably, the water vapor is supplied via saturated air, which is typically supplied under pressure conditions ranging from 0.1 atm to 20 atm (10.1 kPa-a to 2027 kPa-a), preferably from 1 atm to 10 atm (101 kPa-a to

1013 kPa-a), and temperature conditions ranging from 10°C to 600°C, preferably from room temperature to 510°C. For example, the saturated air may be supplied at room temperature and atmospheric pressure. In any embodiment, the gaseous mixture comprising the water vapor is generally supplied at a gas hourly space velocity (GHSV) ranging from 0.1 to 100 hr⁻¹, such as from 0.1 to 10 hr⁻¹. In any embodiment, particularly suitable water vapor partial pressures for use during the steam treatment range from 1 to 50 kPa-a, such as from 1 to 10 kPa-a. Heating of the catalyst precursor to the desired steaming temperature may be conducted at a heating rate of less than 1200°C/hour, such as less than 600°C/hour, but generally in excess of 60°C/hour. The duration of the steam treatment will vary according to the treatment temperature, the GHSV of the gaseous stream comprising the water vapor, and the water vapor partial pressure, but generally varies from 0.5 hours to 24 hours, such as from 1.0 hours to 10 hours.

[0023] Where the hydrogenation component is added to the hydroalkylation catalyst or component thereof as a salt of the desired hydrogenation metal, the non-steamed catalyst precursor or the steamed catalyst will normally undergo an activation step to convert at least part of the metal to its zero-valent elemental state. The activation process is typically conducted by heating in the presence of hydrogen, often in the same reactor as that used for the subsequent hydroalkylation step. However, if desired, the activation may be conducted in one or more separate reactors and the activated catalyst subsequently transferred to the hydroalkylation reactor. Activation is typically conducted at a temperature in a range from 100°C to 260°C.

Hydroalkylation Process

[0024] Hydroalkylation is a two-stage catalytic reaction in which an aromatic compound is partially hydrogenated to produce a cyclic olefin, which then reacts, *in situ*, with the aromatic compound to produce a cycloalkylaromatic product. In the present process, the aromatic compound comprises toluene and/or xylene and the cycloalkylaromatic product comprises a mixture of methylcyclohexyltoluene and/or dimethylcyclohexylxylene isomers. In the case of toluene, the desired reaction may be summarized as follows:



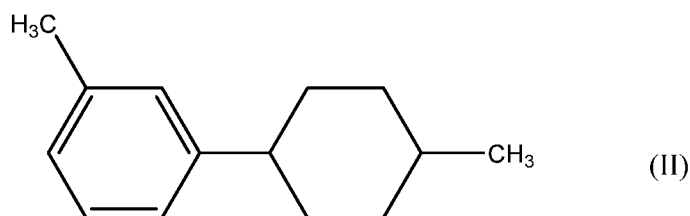
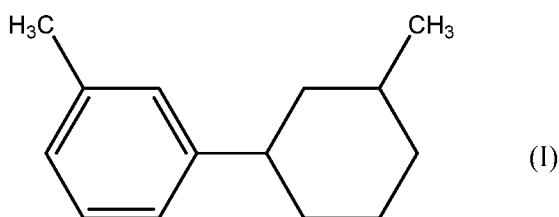
[0025] In addition to the toluene and/or xylene and hydrogen, a diluent, which is

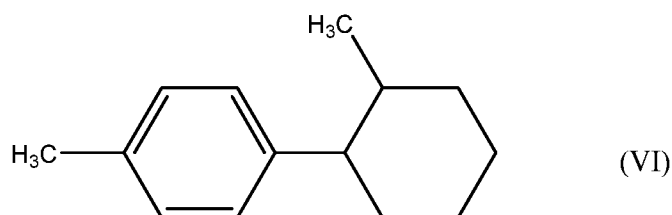
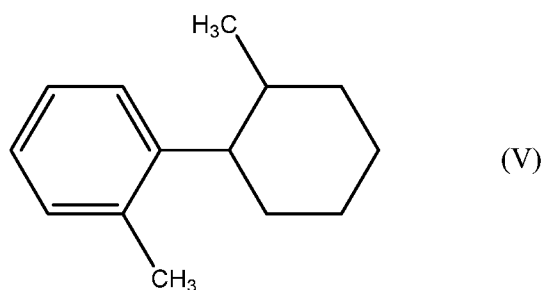
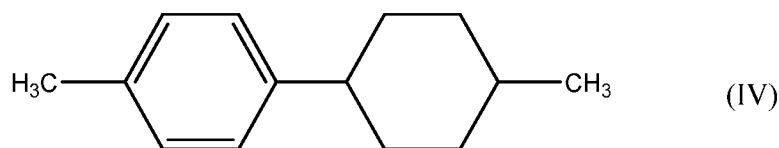
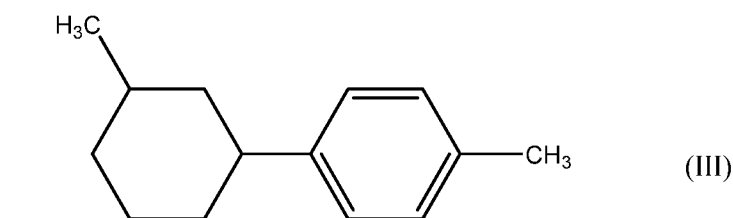
substantially inert under hydroalkylation conditions, may be included in the feed to the hydroalkylation reaction. Often, the diluent is a hydrocarbon, in which the desired cycloalkylaromatic product is soluble, such as a straight chain paraffinic hydrocarbon, a branched chain paraffinic hydrocarbon, and/or a cyclic paraffinic hydrocarbon. Examples of suitable diluents are decane and cyclohexane. Although the amount of diluent is not narrowly defined, desirably the diluent is added in an amount such that the weight ratio of the diluent to the aromatic compound is at least 1:100; for example at least 1: 10, but no more than 10:1, desirably no more than 4:1.

[0026] Optionally, the aromatic feed to the hydroalkylation reaction also includes benzene and/or one or more alkylbenzenes different from toluene and xylene. Suitable alkylbenzenes may have one or more alkyl groups with up to 4 carbon atoms and include, by way of example, ethylbenzene, cumene, and unseparated C₆-C₈ or C₇-C₈ or C₇-C₉ streams.

[0027] The hydroalkylation reaction can be conducted in a wide range of reactor configurations including fixed bed, slurry reactors, and/or catalytic distillation towers. In addition, the hydroalkylation reaction can be conducted in a single reaction zone or in a plurality of reaction zones, in which at least the hydrogen is introduced to the reaction in stages. Suitable reaction temperatures are between 100°C and 400°C, such as between 125°C and 250°C, while suitable reaction pressures are between 100 and 7,000 kPa-a, such as between 500 and 5,000 kPa-a. The molar ratio of hydrogen to aromatic feed is typically from 0.15:1 to 15:1.

[0028] Depending on the feed to the hydroalkylation reaction, the product is a mixture of isomers of methylcyclohexyltoluene isomers (feed comprising toluene) and/or dimethylcyclohexylxylene isomers (feed comprising xylene). For example, in the case of a toluene containing feed, the product comprises a mixture of the following isomers:





5 **[0029]** Of the above isomers, 3,4'-, 4,3'- and 4,4'- methylcyclohexyltoluene (see formulas II-IV) are particularly preferred since 3,4'- and 4,4'-biphenyldicarboxylic are the most desirable precursors to polyesters and plasticizers. According to the present disclosure it has now been found that controlled steaming of the hydroalkylation catalysts as described above results in a higher conversion of toluene to MCH and MCHT.

10 **[0030]** Among the reactions competing with hydroalkylation to MCHT is dialkylation in which the (methylcyclohexyl)toluene product reacts with further methylcyclohexene to produce di(methylcyclohexyl)toluene. Again this by-product can be converted back to (methylcyclohexyl)toluene, in this case by transalkylation. However, this process requires the use of an acid catalyst at temperatures above 160°C and can lead to the production of additional

15 by-products, such as di(methylcyclopentyl)toluenes, cyclohexylxylenes and cyclohexylbenzene. It is therefore desirable to employ a hydroalkylation catalyst that exhibits low selectivity towards di(methylcyclohexyl)toluene and other heavy by-products. Using the steamed catalyst described herein, especially where the acidic component comprises an MCM-22 family molecular sieve, the hydroalkylation reaction product with a toluene feed may

20 contain less than 20 wt% of compounds containing in excess of 14 carbon atoms and with a

xylene feed may contain less than 20 wt% of compounds containing in excess of 16 carbon atoms. Additionally or alternatively, the hydroalkylation reaction product with a toluene feed may contain less than 40 wt% of methylcyclohexane and less than 70 wt% of dimethylbi(cyclohexane) compounds.

5 Dehydrogenation of Hydroalkylation Product

[0031] The major components of the hydroalkylation reaction effluent are (methylcyclohexyl)toluenes and/or (dimethylcyclohexyl)xlenes, unreacted aromatic feed (toluene and/or xylene) and fully saturated single ring by-products (methylcyclohexane and dimethylcyclohexane). The unreacted feed and light by-products can readily be removed from
10 the reaction effluent by, for example, distillation. The unreacted feed can then be recycled to the hydroalkylation reactor, while the saturated by-products can be dehydrogenated to produce additional recyclable feed.

[0032] The remainder of the hydroalkylation reaction effluent, composed mainly of (methylcyclohexyl)toluenes and/or (dimethylcyclohexyl)xlenes, is then dehydrogenated to
15 produce the corresponding methyl-substituted biphenyl compounds. The dehydrogenation is conveniently conducted at a temperature from 200°C to 600°C and a pressure from 100 kPa to 3550 kPa-a (atmospheric to 500 psig) in the presence of dehydrogenation catalyst. A suitable dehydrogenation catalyst comprises one or more elements or compounds thereof selected from Group 10 of the Periodic Table of Elements, for example platinum, on a support, such as silica,
20 alumina or carbon nanotubes. In one embodiment, the Group 10 element is present in amount from 0.1 to 5 wt % of the catalyst. In some cases, the dehydrogenation catalyst may also include tin or a tin compound to improve the selectivity to the desired methyl-substituted biphenyl product. In one embodiment, the tin is present in amount from 0.05 to 2.5 wt % of the catalyst.

25 [0033] Particularly using an MCM-22 family-based catalyst for the upstream hydroalkylation reaction, the product of the dehydrogenation step comprises methyl-substituted biphenyl compounds in which the concentration of the 3,3-, 3,4- and 4,4-dimethyl isomers is at least 50 wt%, such as at least 60 wt%, for example at least 70 wt% based on the total weight of methyl-substituted biphenyl isomers. In addition, the product may contain less
30 than 10 wt%, such as less than 5 wt%, for example less than 3 wt% of methyl biphenyl compounds and less than 5 wt%, such as less than 3 wt%, for example less than 1 wt% of fluorene and methyl fluorenes combined.

Production of Biphenyl Esters and/or Polyesters

[0034] The methyl-substituted biphenyl compounds produced by the dehydrogenation

reaction can readily be converted to ester plasticizers or polyesters by a process comprising oxidation to produce the corresponding carboxylic acids followed by esterification with an alcohol to produce biphenyl esters or reaction with one or more diols to produce polyesters.

[0035] The oxidation can be performed by any process known in the art, such as by reacting
5 the methyl-substituted biphenyl compounds with an oxidant, such as oxygen, ozone or air, or any other oxygen source, such as hydrogen peroxide, in the presence of a catalyst at temperatures from 30°C to 300°C, such as from 60°C to 200°C. Suitable catalysts comprise Co or Mn or a combination of both metals. The oxidation product generally comprises a mixture of biphenylcarboxylic acids, including the desired biphenyl-3,4'-dicarboxylic acid and
10 biphenyl-4,4'-dicarboxylic acid. Often, the oxidation is conducted in the presence of p-xylene such that the oxidation product also comprises terephthalic acid.

[0036] The resulting carboxylic acids can then be esterified to produce biphenyl ester plasticizers by reaction with one or more alcohols or diols, especially those having from 4 to 14 carbon atoms. Suitable esterification conditions are well-known in the art and include, but
15 are not limited to, temperatures of 0 to 300°C and the presence or absence of homogeneous or heterogeneous esterification catalysts, such as Lewis or Bronsted acid catalysts. Suitable alcohols are "oxo-alcohols", by which is meant an organic alcohol, or mixture of organic alcohols, which is prepared by hydroformylating an olefin, followed by hydrogenation to form the alcohols. Typically, the olefin is formed by light olefin oligomerization over heterogeneous
20 acid catalysts, which olefins are readily available from refinery processing operations. The reaction results in mixtures of longer-chain, branched olefins, which subsequently form longer chain, branched alcohols, as described in U.S. Pat. No. 6,274,756, incorporated herein by reference in its entirety. Another source of olefins used in the OXO process are through the oligomerization of ethylene, producing mixtures of predominately straight chain alcohols with
25 lesser amounts of lightly branched alcohols. The biphenyl ester plasticizers of the present application find use in a number of different polymers, such as vinyl chloride resins, polyesters, polyurethanes, ethylene-vinyl acetate copolymers, rubbers, poly(meth)acrylics and mixtures thereof.

[0037] Alternatively, the resulting carboxylic acids can be reacted with one or more diols
30 and optionally with co-produced, or separately added terephthalic acid to produce polyesters by any known method. In any embodiment, the biphenyl dicarboxylic acids may be substituted by the corresponding biphenyl dicarboxylates (esters of corresponding biphenyl dicarboxylic acids). Suitable diols for reaction with the above-mentioned carboxylic acids or dicarboxylates include alkanediols having 2 to 12 carbon atoms, such as monoethylene glycol, diethylene

glycol, 1,3-propanediol, or 1,4-butane diol, 1,6-hexanediol, and 1,4-cyclohexanedimethanol.

[0038] The polyesters may be prepared by conventional direct esterification or transesterification methods. Suitable catalysts include but not limited to titanium alkoxides such as titanium tetraisopropoxide, dialkyl tin oxides, antimony trioxide, manganese (II) acetate and Lewis acids. Suitable conditions include a temperature 170 to 350°C for a time from 0.5 hours to 10 hours. Generally, the reaction is conducted in the molten state and so the temperature is selected to be above the melting point of the monomer mixture but below the decomposition temperature of the polymer. A higher reaction temperature is therefore needed for higher percentages of biphenyl dicarboxylic acid in the monomer mixture. The polyester may be first prepared in the molten state followed by a solid state polymerization to increase its molecular weight or intrinsic viscosity for applications like bottles.

[0039] The invention will now be more particularly described with reference to the following non-limiting Examples and the accompanying drawings.

Example 1: Preparation of Catalysts

[0040] 80 parts MCM-49 zeolite crystals were combined with 20 parts pseudoboehmite alumina, on a calcined dry weight basis. The MCM-49 and pseudoboehmite alumina dry powder were placed in a muller and mixed for 10 to 30 minutes. Sufficient water and 0.05% polyvinyl alcohol were added to the MCM-49 and alumina during the mixing process to produce an extrudable paste. The extrudable paste was formed into a 1/20 inch (0.13 cm) quadrulobe extrudate using an extruder and the resulting extrudate was dried at a temperature ranging from 250°F to 325°F (120°C to 163°C). After drying, the dried extrudate was heated to 1000°F (538°C) under flowing nitrogen. The extrudate was then cooled to ambient temperature and humidified with water saturated air.

[0041] After the humidification, the extrudate was ion exchanged twice with 0.5 to 1 N ammonium nitrate solution. The ammonium nitrate exchanged extrudate was then washed with deionized water to remove residual nitrate prior to calcination in air. After washing, the wet extrudate was dried. The exchanged and dried extrudate was then calcined in a nitrogen/air mixture to a temperature 1000°F (538°C). Afterwards, the calcined extrudate was cooled to room temperature. The 80% MCM-49, 20% Al₂O₃ extrudate was then impregnated with a palladium (II) chloride solution (target: 0.15% Pd) by incipient wetness and then dried overnight at 121°C. The dried catalyst was calcined in air at the following conditions: 5 volumes air per volume catalyst per minute, ramp from room temperature to 538°C at 1°C/min and hold for 3 hours. A portion of the dried catalyst was subsequently ramped from room temperature to 950°F (510°C) at 3°C/min (180°C/hour) and steam treated at 950°F (510°C) for

2 hours by passing a stream of air saturated with water (as determined at room temperature and ambient pressure) through the bed of dried catalyst at a GHSV of 1 hr^{-1} . The steam treated catalyst was labeled as Catalyst A, whereas the remainder of the dried, non-steamed catalyst was labeled as Catalyst B.

5 Example 2: Catalyst Testing in Toluene Hydroalkylation

[0042] Each of the Catalysts A and B was then tested in the hydroalkylation of a toluene feed using the reactor and process described below.

[0043] The reactor unit comprised 24 identical fixed bed reactors. Each reactor comprised a stainless steel tube having an internal diameter of 7 mm and a catalyst bed length of approximately 150 mm, which was placed in the isothermal zone of the furnace. A 2 mm stainless steel thermo-well was placed in the catalyst bed to monitor temperature throughout the catalyst bed using a movable thermocouple.

[0044] Each catalyst was sized to 40/30 sieve mesh, dispersed with quartz chips (20/40 mesh) then loaded into the reactor from the top. The catalyst bed used was typically 15 cm. in length with a typical catalyst load of 0.1 – 2.0 g. The remaining void space at the top of the reactor was filled with quartz chips, with a ¼ plug of glass wool placed on top of the catalyst bed being used to separate quartz chips from the catalyst. The reactor was installed in a furnace with the catalyst bed in the middle of the furnace at a pre-marked isothermal zone. The reactor was then pressure and leak tested typically at 300 psig (2170 kPa-a).

[0045] Each catalyst was pre-conditioned in situ by heating to 25°C to 240°C with H_2 flow at 100 cc/min and holding for 12 hours. A 500 cc ISCO syringe pump was used to introduce a chemical grade toluene feed to the reactor. The feed was pumped through a vaporizer before flowing through heated lines to the reactor. A Brooks mass flow controller was used to set the hydrogen flow rate. A Grove “Mity Mite” back pressure controller was used to control the reactor pressure typically at 150 psig (1135 kPa-a). GC analyses were taken to verify feed composition. The feed was then pumped through the catalyst bed held at the reaction temperature of 120°C to 180°C at a weight hourly space velocity (WHSV) of 1.6 - 10 and a pressure of 10 – 15 barg. The liquid products exiting the reactor flowed through heated lines routed to two collection pots in series, the first pot being heated to 60°C and the second pot cooled with chilled coolant to 10°C. Material balances were taken at 12 to 24 hrs intervals. Samples were taken and diluted with 50% ethanol for analysis. An Agilent 7890 gas chromatograph with FID detector was used for the analysis. The non-condensable gas products were routed to an on line HP 5890 GC. The analysis was done on an Agilent 7890 GC with 150 vial sample tray using the following procedure:

- Inlet Temp: 220°C
- Detector Temp: 240°C (Col + make up = constant)
- Temp Program: Initial temp 120°C hold for 15 min., ramp at 2°C/min to 180°C, hold 15 min; ramp at 3°C/min. to 220°C and hold till end.
- 5 • Column Flow: 2.25 ml/min. (27 cm/sec); Split mode, Split ratio 100:1
- Injector: Auto sampler (0.2 µl).
- Column Parameters:
- Two columns joined to make 120 Meters (coupled with Agilent ultimate union, deactivated.
- 10 • Column # Front end: Supelco β-Dex 120 ; 60 m x 0.25 mm x 0.25 µm film joined to Column # 2 back end: γ-Dex 325: 60 m x 0.25 mm x 0.25 µm film.

[0046] The results of the hydroalkylation testing are summarized in Fig. 1 and Fig. 2.

[0047] Fig. 1 shows that at temperatures of 120, 140, and 160°C, a pressure of 10 bar, a WHSV of 2, and a H₂:hydrocarbon molar ratio of 1, the steamed catalyst A exhibited a higher toluene conversion than Catalyst B. For example, at 160°C, Catalyst A exhibited a toluene conversion in excess of 60 wt% as compared to less than 40 wt% for the non-steamed Catalyst B. Under all tested conditions, Catalyst A also exhibited a lower dialkylate selectivity than Catalyst B.

[0048] Fig. 2 compares the MCHT isomer selectivity of catalysts A and B at temperatures of 120, 140, 160°C, a pressure of 10 bar, a WHSV of 2, and a H₂:hydrocarbon molar ratio of 1. At higher temperatures, the steamed catalyst A exhibited slightly higher selectivity to 4,4'-MCHT, and slightly lower selectivity to 3,4'- and 4,3'-MCHTs, as compared to Catalyst B.

[0049] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

CLAIMS

1. A process for preparing a hydroalkylation catalyst, the process comprising:
 - (a) providing a hydroalkylation catalyst precursor comprising an acidic component
5 and a hydrogenation component; and
 - (b) treating the catalyst precursor in the presence of water vapor at a temperature ranging from 200°C to 600°C to obtain the hydroalkylation catalyst.
2. The process of claim 1, wherein a gaseous stream comprising said water vapor is
10 supplied during the treating step (b) at a gas hourly space velocity (GHSV) ranging from 0.1 to 100 hr⁻¹.
3. The process of claim 2, wherein said gaseous stream comprises saturated air.
- 15 4. The process of claim 3, wherein said saturated air is supplied to the treating step (b) under conditions comprising a pressure ranging from 0.1 atm to 20 atm (10.1 kPa-a to 2027 kPa-a) and a temperature ranging from 10°C to 600°C.
5. The process of any one of the preceding claims, wherein the treating step (b) is
20 conducted at a water vapor partial pressure in a range from 1 to 50 kPa-a.
6. The process of any one of the preceding claims, further comprising:
 - (c) heating the catalyst precursor at a heating rate of less than 1200°C/hour to the
25 temperature of the treating step (b).
7. The process of any one of the preceding claims, wherein the treating step (b) is conducted from 0.5 hours to 24 hours.
8. The process of any one of the preceding claims, wherein the acidic component
30 comprises a molecular sieve.
9. The process of claim 8, wherein the molecular sieve is selected from the group consisting of BEA, FAU, MTW structure type molecular sieves, molecular sieves of the MCM-22 family, and mixtures and combinations thereof.

10. The process of claim 8, wherein the molecular sieve comprises a molecular sieve of the MCM-22 family.
- 5 11. The process of any one of the preceding claims, wherein the hydrogenation component is selected from the group consisting of palladium, ruthenium, nickel, zinc, tin, cobalt, and compounds, mixtures, and combinations thereof.
12. A process for producing one or more cycloalkylaromatic compounds, the process
10 comprising contacting a feed comprising at least one aromatic hydrocarbon selected from the group consisting of toluene, xylene, and mixtures thereof with hydrogen in the presence of the hydroalkylation catalyst prepared using a process according to any one of the preceding claims under conditions effective to produce a hydroalkylation reaction product comprising (methylcyclohexyl)toluenes and/or (dimethylcyclohexyl)xlenes.
- 15 13. A process for producing one or more biphenyl compounds, the process comprising:
(a) contacting a feed comprising at least one aromatic hydrocarbon selected from the group consisting of toluene, xylene, and mixtures thereof with hydrogen in the presence of the hydroalkylation catalyst prepared using a process according
20 to any one of claims 1 to 11 under conditions effective to produce a hydroalkylation reaction product comprising (methylcyclohexyl)toluenes and/or (dimethylcyclohexyl)xlenes; and
(b) dehydrogenating at least part of the hydroalkylation reaction product in the presence of a dehydrogenation catalyst under conditions effective to produce a
25 dehydrogenation reaction product comprising a mixture of methyl-substituted biphenyl compounds.
14. The process of claim 13, wherein the conditions in the contacting (a) include a temperature from 100°C to 400°C and a pressure from 100 to 7,000 kPa-a.
- 30 15. The process of claim 13 or claim 14, wherein the molar ratio of hydrogen to aromatic feed supplied to the contacting (a) is from 0.15:1 to 15:1.

16. The process of any one of claims 12 to 15, wherein the aromatic hydrocarbon is toluene and the hydroalkylation reaction product comprises less than 40 wt% of methylcyclohexane and less than 70 wt% of dimethylbi(cyclohexane) compounds.
- 5 17. The process of any one of claims 12 to 16, wherein the aromatic hydrocarbon is toluene and the hydroalkylation reaction product comprises less than 20 wt% of compounds containing in excess of 14 carbon atoms.
18. The process of any one of claims 12 to 15, wherein the aromatic hydrocarbon is xylene
10 and the hydroalkylation reaction product comprises less than 20 wt% of compounds containing in excess of 16 carbon atoms.
19. The process of any one of claims 12 to 18, wherein the feed further comprises benzene and/or at least one alkylbenzene different from toluene and xylene.
- 15 20. The process of any one of claims 13 to 18, wherein the dehydrogenation catalyst comprises an element or compound thereof selected from Group 10 of the Periodic Table of Elements.
- 20 21. The process of any one of claims 13 to 20, wherein the dehydrogenation conditions in (b) include a temperature from 200°C to 600°C and a pressure from 100 kPa-a to 3550 kPa-a (atmospheric to 500 psig).
22. The process of any one of claims 13 to 21, further comprising:
25 (c) oxidizing at least part of the dehydrogenation reaction product to produce an oxidation product comprising biphenyl-4,4'-dicarboxylic acid.
23. The process of claim 22, wherein the oxidizing (c) is conducted in the presence of p-xylene such that the oxidation product also comprises terephthalic acid.
- 30 24. The process of claim 22 or claim 23, further comprising:
(d) reacting the biphenyl carboxylic acids with one or more C₄ to C₁₄ alcohols under conditions effective to produce biphenyl esters.
25. The process of claim 22 or claim 23, further comprising:

- (e) reacting at least part of the oxidation product with a diol to produce a polyester product.

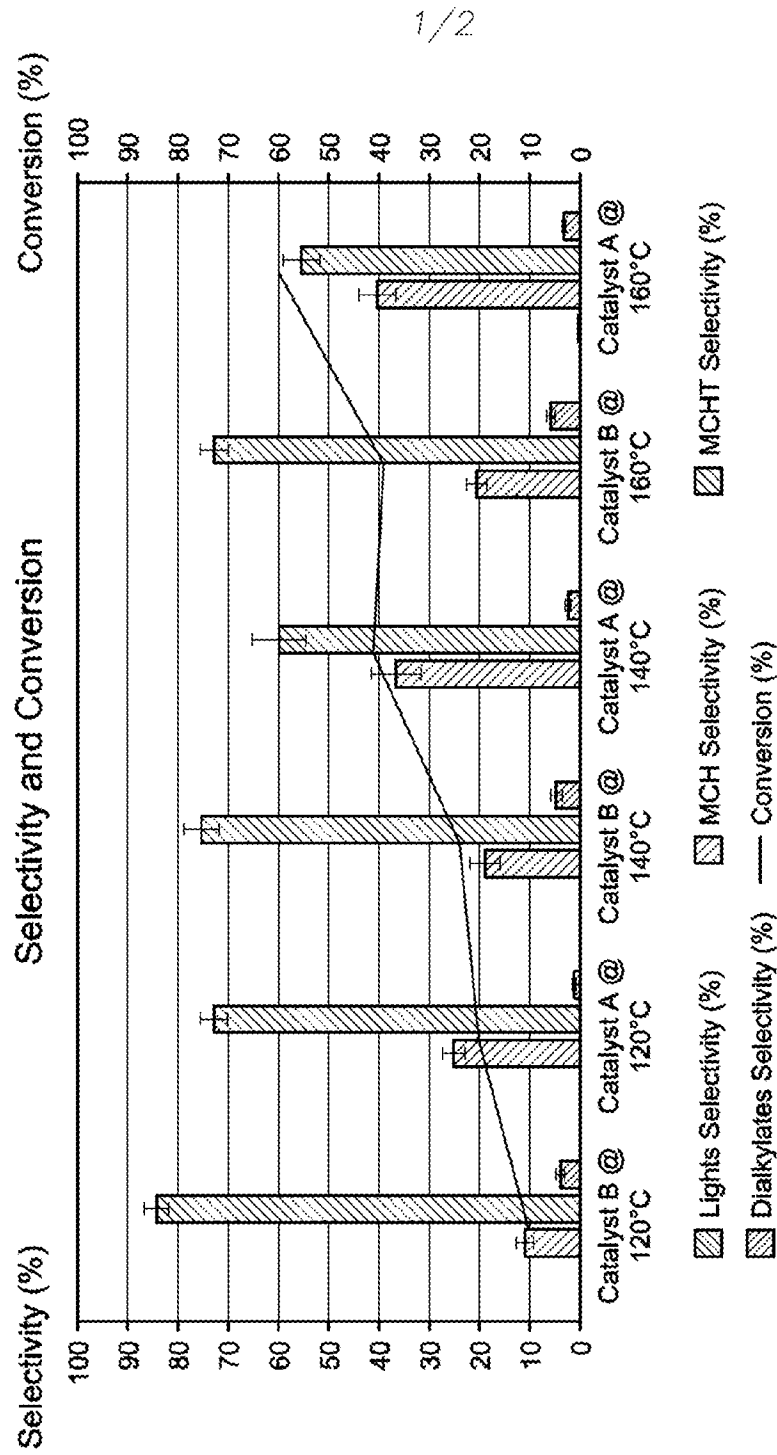


FIG. 1

2/2

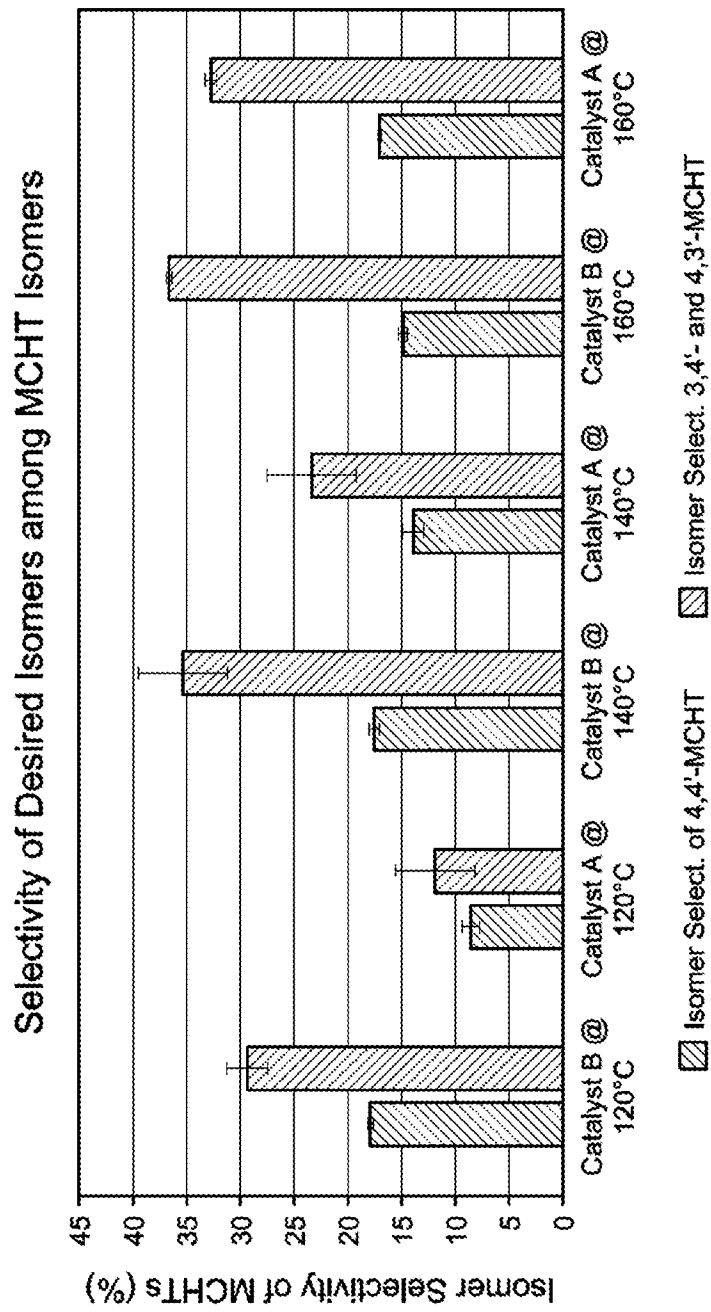


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/028503

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J29/74 B01J29/12 B01J29/03 C07C2/74 C07C5/367
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 3 760 019 A (CRONE J ET AL) 18 September 1973 (1973-09-18) abstract column 2, lines 17-62 example 3	1-11
X	----- US 2014/275609 A1 (DAKKA JIHAD M [US] ET AL) 18 September 2014 (2014-09-18) cited in the application abstract example 1	1-11
X	----- EP 2 878 590 A1 (DALIAN CHEMICAL PHYSICS INST [CN]) 3 June 2015 (2015-06-03) abstract example 9 ----- -/-	1-8,11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

5 August 2019

Date of mailing of the international search report

08/10/2019

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/028503

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/025283 A1 (CHENG JANE C [US] ET AL) 22 January 2015 (2015-01-22) abstract example 8 -----	1-8,11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/028503

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-11

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11

A process for preparing a hydroalkylation catalyst, the process comprising:

- a) providing a hydroalkylation catalyst precursor comprising an acidic component and a hydrogenation component; and
- b) treating the catalyst precursor in the presence of water vapor at a temperature ranging from 200 °C to 600 °C to obtain the hydroalkylation catalyst

2. claims: 12(completely); 16-19(partially)

A process for producing one or more cycloalkylaromatic compounds, the process comprising contacting a feed comprising at least one aromatic hydrocarbon selected from the group consisting of toluene, xylene, and mixtures thereof with hydrogen in the presence of the hydroalkylation catalyst prepared using a process according to any one of the preceding claims under conditions effective to produce a hydroalkylation reaction product comprising (methylcyclohexyl)toluenes and/or (dimethylcyclohexyl)xylenes.

3. claims: 13-15, 20-25(completely); 16-19(partially)

A process for producing one or more biphenyl compounds, the process comprising:(a) contacting a feed comprising at least one aromatic hydrocarbon selected from the group consisting of toluene, xylene, and mixtures thereof with hydrogen in the presence of the hydroalkylation catalyst prepared using a process according to any one of claims 1 to 11 under conditions effective to produce a hydroalkylation reaction product comprising (methylcyclohexyl)toluenes and/or (dimethylcyclohexyl)xylenes; and(b) dehydrogenating at least part of the hydroalkylation reaction product in the presence of a dehydrogenation catalyst under conditions effective to produce a dehydrogenation reaction product comprising a mixture of methyl-substituted biphenyl compounds.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2019/028503

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