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(54) Title: ACTIVATION OF DEHYDROGENATION CATALYSTS

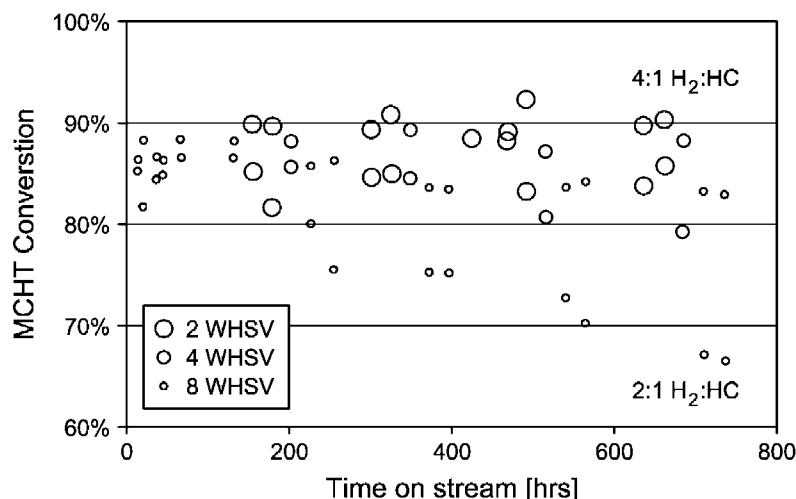


FIG. 1

(57) Abstract: In a process for dehydrogenating cyclohexylbenzene and/or alkyl-substituted cyclohexylbenzene compounds, a dehydrogenation catalyst comprising at least one Group 10 metal compound on a support is heated in the presence of hydrogen from a first temperature from 0°C to 200°C to a second, higher temperature from 60°C to 500°C at a ramp rate no more than 100°C/hour. The dehydrogenation catalyst is contacted with hydrogen at the second temperature for a time from 3 to 300 hours to produce an activated dehydrogenation catalyst. A feed comprising cyclohexylbenzene and/or an alkyl-substituted cyclohexylbenzene compound is then contacted with hydrogen in the presence of the activated dehydrogenation catalyst under conditions effective to produce a dehydrogenation reaction product comprising biphenyl and/or an alkyl-substituted biphenyl compound.



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TITLE: ACTIVATION OF DEHYDROGENATION CATALYSTS

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PRIORITY

- 5 [0001] This invention claims priority to and the benefit of USSN 62/068,144, filed October 24, 2014, and EP application 14195868.6, filed December 2, 2014.

FIELD OF THE INVENTION

[0002] This disclosure relates to activation of dehydrogenation catalysts useful in the production of methylbiphenyl compounds.

10 **BACKGROUND OF THE INVENTION**

[0003] Methylbiphenyl compounds are useful intermediates in the production of a variety of commercially valuable products, including polyesters and plasticizers for PVC and other polymer compositions. For example, they can be converted to an ester plasticizer by a process comprising oxidation to produce the corresponding mono- or dicarboxylic acid
15 followed by esterification of the acid function with a long chain alcohol. In addition, diphenyl-4,4'-dicarboxylic acid, optionally together with diphenyl-3,4'-dicarboxylic acid, is a potential precursor, either alone or as a modifier for polyethylene terephthalate (PET), in the production of polyester fibers, engineering plastics, liquid crystal polymers for electronic and mechanical devices, and films with high heat resistance and strength.

20 [0004] As disclosed in our co-pending US Patent Application Serial Numbers 14/201,287 and 14/201,224, both filed March 7, 2014 and incorporated herein by reference, dimethylbiphenyl compounds may be produced by hydroalkylation of toluene followed by dehydrogenation of the resulting (methylcyclohexyl)toluene (MCHT). An alternative route via benzene is described in our co-pending US Patent Application Serial Number 14/164,889,
25 filed January 27, 2014 and also incorporated herein by reference. In this alternative route, the benzene is initially hydroalkylated to cyclohexylbenzene (CHB), which is then dehydrogenated to biphenyl. The biphenyl is subsequently alkylated with methanol to produce the desired methylbiphenyl compounds.

[0005] One problem with both of these routes for producing methylbiphenyl compounds
30 is that the catalyst employed in the dehydrogenation step tends to undergo rapid deactivation. There is therefore interest in developing an improved dehydrogenation catalyst that exhibits enhanced stability when employed in the dehydrogenation of MCHT and and/or CHB.

SUMMARY OF THE INVENTION

[0006] According to the present invention, it has now surprisingly been found that the stability of MCHT and CHB dehydrogenation catalysts can be improved by controlling certain conditions, such as the temperature ramp rate, the final temperature and the hydrogen
5 feed rate, used to activate the catalyst. In addition, further improvements in catalyst stability can be achieved by controlling the dehydrogenation conditions and/or by reducing or eliminating the amount of heavy compounds, particularly, dicyclohexylbenzene compounds, in the dehydrogenation feed.

[0007] In one aspect, the invention resides in a process for dehydrogenating
10 cyclohexylbenzene and/or alkyl-substituted cyclohexylbenzene compounds, the process comprising:

- (a) providing a dehydrogenation catalyst comprising at least one Group 10 metal compound on a support;
- (b) heating the dehydrogenation catalyst in the presence of hydrogen from a first
15 temperature from 0°C to 200°C to a second, higher temperature from 60°C to 500°C at a ramp rate no more than 100°C/hour;
- (c) contacting the dehydrogenation catalyst with hydrogen at the second temperature for a time from 3 to 300 hours to produce an activated dehydrogenation catalyst; and
- (d) contacting a feed comprising cyclohexylbenzene and/or an alkyl-substituted
20 cyclohexylbenzene compound with hydrogen in the presence of the activated dehydrogenation catalyst under conditions effective to produce a dehydrogenation reaction product comprising biphenyl and/or an alkyl-substituted biphenyl compound.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figure 1 is a graph of weight % conversion of methylcyclohexyltoluene (MCHT)
25 against time on stream at a temperature of 430°C and varying WHSV and H₂/HC values (molar) for the process of Example 4.

[0009] Figure 2 is a graph of weight % conversion of methylcyclohexyltoluene (MCHT) against time on stream at a WHSV of 16 and H₂/HC of 4 (molar) and varying temperatures (in ascending order of 350°C, 375°C, 400°C, and 430°C) for the process of Example 4.

[0010] Figure 3 is a graph comparing weight % conversion of the dehydrogenation feed
30 against time on stream at a temperature of 430°C, a pressure of 100 psig (791 kPa-a), WHSV of 2 and H₂/HC of 2:1 (molar) for the processes of Examples 4 and 5.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0011] An improved process is described for activating and operating catalysts useful for

the dehydrogenation of cyclohexylbenzene and/or alkyl-substituted cyclohexylbenzene compounds. As used herein, the term "alkyl-substituted cyclohexylbenzene" is intended to include cyclohexylbenzene compounds having one or more alkyl substituents on either the cyclohexane ring or the benzene ring or both. Thus, for example, suitable alkyl-substituted cyclohexylbenzene compounds for use in the present process include methylcyclohexylbenzene, cyclohexyltoluene, (methylcyclohexyl)toluene and dimethylcyclohexylxylenes. As will be discussed in more detail below such compounds can be produced by hydroalkylation of one or more of benzene, toluene and xylenes, including combinations of such C₆-C₈ aromatics, as well as by certain transalkylation reactions.

10 **Dehydrogenation Catalyst**

[0012] A suitable dehydrogenation catalyst for use in the present process comprises one or more elements or compounds thereof selected from Group 10 of the Periodic Table of Elements, for example nickel, palladium, platinum, preferably platinum, on a refractory support. In one embodiment, the Group 10 element is present in an amount from 0.1 to 5 wt % of the catalyst. In some cases, the dehydrogenation catalyst may also include tin or a tin compound. In one embodiment, the tin is present in an amount from 0.1 to 5 wt %, such as from 0.05 to 2.5 wt %, of the catalyst.

[0013] As used herein, the numbering scheme for the Periodic Table Groups is the New notation as described in Chemical and Engineering News, 63(5), 27 (1985).

20 [0014] The support employed in the dehydrogenation catalyst is refractory in the sense that it is capable of withstanding the conditions employed in the dehydrogenation reaction without physical or chemical changes. Non-limiting examples of suitable refractory support materials include: alumina, silica, silica-alumina, titania, calcium oxide, strontium oxide, barium oxide, magnesium oxide, carbon, zirconia, diatomaceous earth, lanthanide oxides including cerium oxide, lanthanum oxide, neodymium oxide, yttrium oxide and praseodymium oxide, oxides of chromium, thorium, uranium, niobium and tantalum, tin oxide, zinc oxide, and aluminum phosphate.

[0015] In one embodiment, the refractory support is selected to have one or more, such as two or more, and desirably all, of the following acidic properties:

- 30 (i) an alpha value between 0.1 to 10, preferably less than 1;
- (ii) a combined Bronsted and Lewis acid activity from 0.1 to 0.5 mmol/gm of the dehydrogenation catalyst, preferably about 0.1 mmol/gm; and
- (iii) a temperature programmed ammonia adsorption from 0.1 to 1 mmol/gm of the dehydrogenation catalyst, preferably about 0.1 mmol/gm.

[0016] Alpha value is a measure of the cracking activity of an acid catalyst and is described in U.S. Patent No. 3,354,078 and in the Journal of Catalysis, Vol. 4, p. 527 (1965); Vol. 6, p. 278 (1966); and Vol. 61, p. 395 (1980), each incorporated herein by reference as to that description. The experimental conditions of the test used herein include a constant
 5 temperature of 538°C and a variable flow rate as described in detail in the Journal of Catalysis, Vol. 61, page 395.

[0017] The Bronsted and Lewis acid activities of an acidic material can be determined from the amount of pyridine adsorbed by the material. Such a test can be conducted by grinding the material to a size of less than 100 mesh and then pressing the ground material
 10 into a thin self-supporting wafer typically having a weight from 10 ~15 mg/cm². The wafer is then placed in an IR transmission cell equipped with CaF₂ windows and the wafer is pre-calcined in vacuum at 450°C for 1.5 hr. The adsorption of pyridine is carried out at 250°C from a glass vial attached to the manifold of the cell. The pyridine partial pressure is measured by a Baratron pressure transducer. The IR bands at 1545 cm⁻¹ and 1450 cm⁻¹ are
 15 used for the quantitative evaluation of Bronsted and Lewis acid sites, respectively. The amount of pyridium ions and Lewis-bonded pyridine per gram of sample can then be calculated using Beer-Lambert's law according to the formula:

$$n/m = (A_i * Q) / (\epsilon_i * m)$$

where A_i is the integrated absorbance [cm⁻¹];

20 ϵ_i is the integrated molar extinction coefficient [cm/μmol];

m is the mass of wafer [g];

Q is the geometric surface area of wafer [cm²]; and

n is the amount of pyridine [μmol].

[0018] Values for the integrated molar extinction coefficients were adopted from the
 25 literature [C.A. Emeis, J. Catal., 141 (1993) 347] to be $\epsilon_B = 1.67$ cm/μmol for pyridium ions, and $\epsilon_L = 2.22$ cm/μmol for Lewis-bonded pyridine.

[0019] The temperature programmed ammonia absorption (TPAA) measures the total number of acid sites in a sample via the formation of an adsorption complex with Bronsted and Lewis acid sites. In the tests cited herein, before the ammonia absorption, each sample
 30 was calcined in air at 500°C for 1 hr to remove any absorbed moisture and volatiles. The sample was cooled down in air to 250°C. Then the system was switched to a helium stream. Recurrent pulses of 1% NH₃/He were added into the system. The sample with ammonia absorption was weighed in-situ by the microbalance to determine the TPAA value in mmol of

NH₃/gm of the sample. After sample acid sites were saturated with NH₃, the system was purged with helium stream to remove physical absorbed ammonia. The system was ramped from 250°C to 500°C with a ramping rate of 5°C/min to generate a programmed ammonia desorption (TPAD) profile.

- 5 [0020] Suitable refractory acidic supports for the dehydrogenation catalyst comprise one or more supports selected from the group consisting of alumina, silica, silica-alumina, titania, calcium oxide, strontium oxide, barium oxide, magnesium oxide, carbon, zirconia, diatomaceous earth, lanthanide oxides including cerium oxide, lanthanum oxide, neodymium oxide, yttrium oxide and praeodymium oxide, oxides of chromium, thorium, uranium, 10 niobium and tantalum, tin oxide, zinc oxide, and aluminum phosphate. A preferred support is alumina.

Preparation and Activation of the Dehydrogenation Catalyst

- [0021] The dehydrogenation catalyst can be produced by any known method of adding a Group 10 metal compound and, where applicable, a tin compound to a refractory support. 15 For example, suitable methods include impregnation, ion exchange and precipitation. In particular, where the dehydrogenation catalyst contains tin, the catalyst may be prepared by impregnating the support with an aqueous solution of a suitable tin compound, such as tin chloride, and/or tin tartrate. The impregnated support containing Sn is then dried in air, such as at 120°C for 4 hrs and, and may then be calcined, such as at 538°C in air for 3 hrs, to 20 convert the tin to an oxide form. Afterwards, Pt may be added to the Sn-containing support by impregnation with an aqueous solution of a suitable platinum compound, such as (NH₃)₄Pt(NO₃)₂. The sample containing Sn and Pt is dried in air, such as at 120°C for 4 hrs, and then calcined, such as at 360°C in air for 3 hrs. Alternatively, the order of impregnation can be reversed (Pt added before the Sn) and a single calcination can be used after addition of 25 both metals.

- [0022] Generally, the resultant catalyst contains the Group 10 metal and, where applicable, tin in an oxidized state and so, before use of the catalyst in the dehydrogenation of cyclohexylbenzene and/or alkyl-substituted cyclohexylbenzene compounds, it is desirable to activate the catalyst to convert the Group 10 metal and/or tin to a reduced form, and generally 30 a zerovalent form. According to the present process, such activation is effected by heating the catalyst, either as-calcined or after an initial drying step, in the presence of hydrogen from a first temperature to a second, higher temperature at a ramp rate no more than 100°C/hour, such as no more than 50°C/hour, for example no more than 20°C/hour. In terms of ranges, the ramp rate for the heating from the first to the second temperature may be from 0.5°C to

100°C/hour, such as from 0.5°C to 50°C/hour, for example from 1°C to 20°C/hour. Preferably the second higher temperature is at least 100°C higher than the first temperature, preferably at least 150°C higher, preferably at least 200°C higher. The catalyst is then reacted with hydrogen at the second temperature for a time from 3 to 300 hours, such as from
5 30 to 150 hours, for example from 40 to 80 hours, sufficient to achieve the required activation.

[0023] In some embodiments, the first temperature in the above activation process is from 0°C to 200°C. Where the activation is conducted without an initial drying step, the first temperature may be at or near ambient temperature, for example, from 0°C to 40°C, such as
10 from 10°C to 30°C. Where the activation is conducted after an initial drying step, the first temperature may be at or near the drying temperature, such as from 60°C to 200°C, for example from 120°C to 150°C.

[0024] In some embodiments, the second temperature in the above activation process is from 60°C to 500°C. Preferred values for the second temperature are from 120°C to 450°C,
15 for example from 200°C to 430°C. The second temperature may be held substantially constant during the activation process or can be varied within the above ranges.

[0025] Hydrogen is supplied to the catalyst during the activation process, that is both during ramping from the first to second temperature and during heating at the second temperature. Hydrogen may also be supplied to the catalyst during any initial drying process.
20 A suitable hydrogen flow rate for the supply of hydrogen during heating at the second temperature is from 10 to 300 sccm/g of catalyst, for example from 100 to 150 sccm/g of catalyst. Similar supply rates apply to the hydrogen fed to the catalyst during the ramping step and the optional drying step.

[0026] The activation process can be conducted in any known form of reactor, such as a
25 fixed bed reactor, a moving bed reactor or a fluidized bed reactor. Preferably, the activation process is conducted *in-situ* in the reactor used in the subsequent dehydrogenation process.

Dehydrogenation Process

[0027] The activated catalyst produced by the present process is found to exhibit excellent activity and stability when used in the dehydrogenation of feeds comprising
30 cyclohexylbenzene and/or alkyl-substituted cyclohexylbenzene compounds. Suitable conditions for the dehydrogenation reaction include a temperature from 200°C to about 600°C and a pressure from 100 kPa-a to 3550 kPa-a, such as a temperature from 200°C to 500°C and a pressure from 100 kPa to 1600 kPa-a, for example a temperature from 350°C to about 450°C

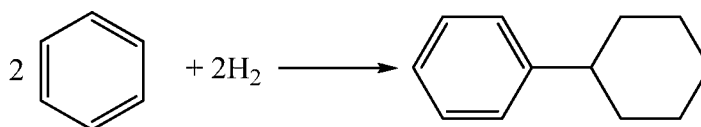
and a pressure from 340 kPa-a to about 1400 kPa-a. The dehydrogenation reaction may be conducted in the presence of hydrogen such that the hydrogen to hydrocarbon molar ratio in the dicyclohexylbenzene compounds feed is in excess of 2, preferably at least 4.

[0028] In some embodiments, it may be desirable to ensure that the dehydrogenation feed comprises less than 0.1 wt% of dicyclohexylbenzene compounds, such as may be present where the feed comprises the effluent from a hydroalkylation process. In such a case, the hydroalkylation effluent may undergo a distillation process to reduce the level of dicyclohexylbenzene compounds to the desired value before the effluent is supplied to the dehydrogenation reaction.

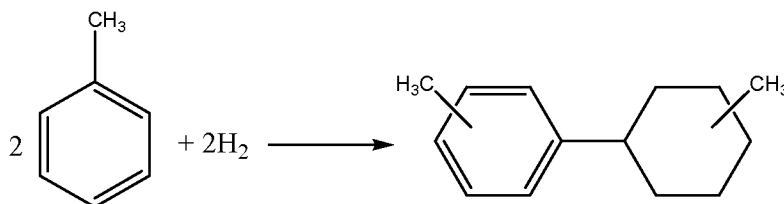
[0029] The dehydrogenation process can be conducted in any known form of reactor, such as a fixed bed reactor, a moving bed reactor, a fluidized bed reactor or a distillation reactor.

Dehydrogenation Feeds

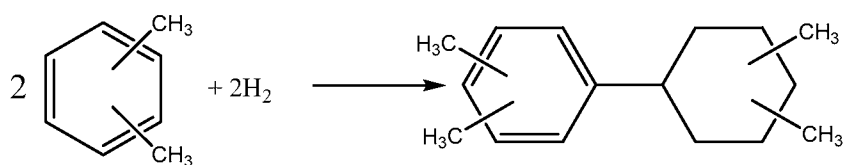
[0030] The activated catalyst produced by the present process can be used in the dehydrogenation of a wide variety of feeds comprising cyclohexylbenzene and/or alkyl-substituted cyclohexylbenzene compounds, especially those obtained by the hydroalkylation of benzene, toluene and/or xylenes. For example, when contacted with a suitable bifunctional catalyst (discussed below) under hydroalkylation conditions, benzene initially undergoes partial hydrogenation to cyclohexene which then alkylates additional benzene to produce cyclohexylbenzene. The overall reaction can be summarized as follows:



[0031] Similarly, in the case of toluene, hydroalkylation yields a mixture of (methylcyclohexyl)toluene isomers according to the reaction:



whereas with xylenes the hydroalkylation produces a mixture of dimethylcyclohexylxylenes according to the reaction:



[0032] Suitable dehydrogenation feeds can also be produced by hydroalkylation of a mixture of two or more of benzene, toluene and/or xylenes. For example, hydroalkylation of a mixture of benzene and toluene produces methylcyclohexylbenzenes and/or cyclohexyltoluenes, in addition to cyclohexylbenzene and (methylcyclohexyl)toluenes.

[0033] Suitable bifunctional catalysts for use in the above hydroalkylation reactions comprise 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 metal oxides. 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 silica, alumina, zirconia, titania, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia.

[0034] Any known hydrogenation metal or compound thereof can be employed as the hydrogenation component of the catalyst, although suitable metals include palladium, ruthenium, nickel, zinc, tin, and cobalt, with palladium being particularly advantageous. In certain embodiments, the amount of hydrogenation metal present in the catalyst is between about 0.05 and about 10 wt%, such as between about 0.1 and about 5 wt%, of the catalyst.

[0035] In one embodiment, the solid acid alkylation component comprises a large pore molecular sieve having a Constraint Index (as defined in U.S. Patent No. 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 U.S. Patent No. 3,923,636. Zeolite ZSM-20 is described in U.S. Patent No. 3,972,983. Zeolite Beta is described in U.S. Patent Nos. 3,308,069 and Re. No. 28,341. Low sodium Ultrastable Y molecular sieve (USY) is described in U.S. Patent Nos. 3,293,192 and

3,449,070. Dealuminized Y zeolite (Deal Y) may be prepared by the method found in U.S. Patent No. 3,442,795. Zeolite UHP-Y is described in U.S. Patent No. 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 U.S. Patent Nos. 3,766,093 and 3,894,104.

[0036] In another, more preferred embodiment, the solid acid alkylation component comprises a molecular sieve of the MCM-22 family. 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.

[0037] Molecular sieves of 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 MCM-22 family include MCM-22 (described in U.S. Patent No. 4,954,325), PSH-3 (described in U.S. Patent No. 4,439,409), SSZ-25 (described in U.S. Patent No. 4,826,667), ERB-1 (described in European Patent No. 0293032), ITQ-1 (described in U.S. Patent No. 6,077,498), ITQ-2 (described in International Patent Publication No.

WO97/17290), MCM-36 (described in U.S. Patent No. 5,250,277), MCM-49 (described in U.S. Patent No. 5,236,575), MCM-56 (described in U.S. Patent No. 5,362,697) and mixtures thereof. Related zeolite UZM-8 is also suitable for use as the hydroalkylation catalyst.

[0038] In addition to the benzene, toluene and/or xylene and hydrogen, a diluent, which is substantially inert under hydroalkylation conditions, may be supplied to the hydroalkylation reaction. In certain embodiments, 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.

[0039] 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 about 100°C and about 400°C, such as between about 125°C and about 250°C, while suitable reaction pressures are between about 100 and about 7,000 kPa, such as between about 500 and about 5,000 kPa. The molar ratio of hydrogen to aromatic feed is typically from about 0.15:1 to about 15:1.

[0040] Although the hydroalkylation reaction is highly selective towards the desired cyclohexylbenzene compounds, the effluent from the hydroalkylation reaction may contain some unreacted benzene, toluene and/or xylene as well as fully saturated and dialkylated by-products. The unreacted aromatic compounds may be recovered by distillation and recycled to the reactor. The remaining effluent from such distillation may be further distilled to separate the monoalkylated products from the dialkylated by-products and other heavies. However, depending on the level of conversion in the hydroalkylation reaction and the amount, if any, of separation of the hydroalkylation effluent, the feed to the present dehydrogenation process may comprise large quantities of the unreacted aromatic starting materials and their fully saturated analogs. For example, where the dehydrogenation feed is produced by hydroalkylation of benzene, the feed may also contain up to 90 wt% benzene and/or cyclohexane. Similarly, where the dehydrogenation feed is produced by hydroalkylation of an alkylated benzene, such as toluene, the feed may also contain up to 90

wt% of the alkylated benzene, such as toluene, and/or the corresponding alkylated cyclohexane, such as methylcyclohexane.

[0041] In another embodiment, the dehydrogenation feed may comprise methylcyclohexylbenzene and/or cyclohexyltoluene produced by the transalkylation of cyclohexylbenzene with toluene. Thus, as discussed above, the production of methylbiphenyl compounds from benzene by hydroalkylation/dehydrogenation requires the addition of methyl group(s) to the biphenyl product of the dehydrogenation stage. This would normally be achieved by alkylation with methanol. However, an attractive alternative route involves transalkylation of cyclohexylbenzene product of the hydroalkylation step with toluene. Such a transalkylation reaction can be conducted in the presence of a solid acid catalyst, such as a molecular sieve and in particular a large pore molecular sieve having a Constraint Index (as defined in U.S. Patent No. 4,016,218) less than 2 and/or a molecular sieve of the MCM-22 family. Suitable conditions for the transalkylation reaction include a temperature from 75°C to 250°C, such as from 100°C to 200°C, for example 125°C to 160°C and a pressure from 100 to 3550 kPa-absolute, such as from 1000 to 1500 kPa-absolute. In some embodiments, the transalkylation reaction may be conducted in the same reactor as the hydroalkylation reaction.

[0042] In another embodiment, this invention relates to:

1. A process for dehydrogenating cyclohexylbenzene and/or alkyl-substituted cyclohexylbenzene compounds, the process comprising:
 - (a) providing a dehydrogenation catalyst comprising at least one Group 10 metal compound on a support;
 - (b) heating the dehydrogenation catalyst in the presence of hydrogen from a first temperature from 0°C to 200°C to a second, higher temperature from 60°C to 500°C at a ramp rate no more than 100°C/hour;
 - (c) contacting the dehydrogenation catalyst with hydrogen at the second temperature for a time from 3 to 300 hours to produce an activated dehydrogenation catalyst; and
 - (d) contacting a feed comprising cyclohexylbenzene and/or an alkyl-substituted cyclohexylbenzene compound with hydrogen in the presence of the activated dehydrogenation catalyst under conditions effective to produce a dehydrogenation reaction product comprising biphenyl and/or an alkyl-substituted biphenyl compound.
2. The process of paragraph 1, wherein the at least one Group 10 metal comprises platinum.
3. The process of paragraph 2, wherein the dehydrogenation catalyst comprises from 0.1

- to 5% wt% of elemental platinum.
4. The process of any of paragraphs 1 to 3, wherein the dehydrogenation catalyst further comprises a tin compound, preferably tin chloride or tin tartrate.
5. The process of paragraph 4, wherein the dehydrogenation catalyst comprises from 0.1 to 5 wt% of elemental tin.
6. The process of any of paragraphs 1 to 5 and further comprising:
- (e) treating a support with a solution containing a Group 10 metal compound in a solvent; and
- (f) removing the solvent from the treated support to produce the dehydrogenation catalyst on a support provided in (a).
7. The process of any of paragraphs 1 to 6, wherein the temperature ramp during the heating (b) is from 0.5°C/hour to 100°C/hour.
8. The process of any of paragraphs 1 to 7, wherein the temperature ramp during the heating (b) is from 0.5°C/hour to 50°C/hour.
9. The process of any of paragraphs 1 to 8, wherein the temperature ramp during the heating (b) is from 1°C/hour to 20°C/hour.
10. The process of any of paragraphs 1 to 9, wherein hydrogen is supplied to the dehydrogenation catalyst at least during the contacting (c) at a rate of 10 to 300 sccm/g of catalyst.
11. The process of any of paragraphs 1 to 10, wherein the conditions in the contacting (d) include a hydrogen to hydrocarbon molar ratio in excess of 2, preferably at least 4.
12. The process of any of paragraphs 1 to 11, wherein the conditions in the contacting (d) include a temperature from 200°C to 500°C and a pressure from 100 kPa to 1600 kPa-a.
13. The process of any of paragraphs 1 to 12, wherein the feed comprises less than 0.1 wt% of dicyclohexylbenzene compounds.
14. The process of any of paragraphs 1 to 13, wherein the feed comprises cyclohexylbenzene produced by the hydroalkylation of benzene.
15. The process of any of paragraphs 1 to 14, wherein the feed comprises (methylcyclohexyl)toluene produced by the hydroalkylation of toluene.
16. The process of any of paragraphs 1 to 15, wherein the feed comprises dimethylcyclohexylxylenes from the hydroalkylation of xylenes.
17. The process of any of paragraphs 1 to 16, wherein the feed comprises methylcyclohexylbenzene and/or cyclohexyltoluene produced from the hydroalkylation of toluene and benzene or the transalkylation of cyclohexylbenzene with toluene.

18. The process of any of paragraphs 1 to 17, wherein the reactor feed also contains up to 90 wt% benzene or cyclohexane.
19. The process of any of paragraphs 1 to 17, wherein the reactor feed also contains up to 90 wt% alkylated benzene or alkylated cyclohexane.
- 5 20. The process of any of paragraphs 1 to 17, wherein the reactor feed also contains up to 90 wt% toluene and/or methylcyclohexane.
21. The process of any of paragraphs 1 to 20, wherein the first temperature is at least 100°C higher than the second temperature in (b).
22. The process of any of paragraphs 1 to 21, wherein the support is selected from the
10 group consisting of alumina, silica, silica-alumina, titania, calcium oxide, strontium oxide, barium oxide, magnesium oxide, carbon, zirconia, diatomaceous earth, lanthanide oxides including cerium oxide, lanthanum oxide, neodymium oxide, yttrium oxide and praesodymium oxide, oxides of chromium, thorium, uranium, niobium and tantalum, tin oxide, zinc oxide, and aluminum phosphate.
- 15 23. The process of any of paragraphs 1 to 22, wherein the feed of (d) comprises less than 0.1 wt% of dicyclohexylbenzene.
24. The process of any of paragraphs 1 to 22, wherein the temperature ramp rate of (b) is 0.5 to 100°C/hour, alternately 0.5 to 50°C/hour, alternately 1 to 20°C/hour.

Experimental

- 20 [0043] The invention will now be more particularly described with reference to the accompanying drawings and the following non-limiting Examples. Unless otherwise indicated, room or ambient temperature is about 23°C.

Example 1: Preparation of 0.3%Pd/MCM-49 Hydroalkylation Catalyst

- 25 [0044] 80 parts MCM-49 zeolite crystals are combined with 20 parts pseudoboehmite alumina on a calcined dry weight basis. The MCM-49 and pseudoboehmite alumina dry powder is placed in a muller or a mixer and mixed for about 10 to 30 minutes. Sufficient water and 0.05% polyvinyl alcohol is added to the MCM-49 and alumina during the mixing process to produce an extrudable paste. The extrudable paste is formed into a 1/20
30 inch diameter quadralobe extrudate using an extruder. After extrusion, the quadralobe extrudate is dried at a temperature ranging from 250°F to 325°F (121 to 163°C). After drying, the dried extrudate is heated to 1000°F (538°C) under flowing nitrogen. The extrudate is then cooled to ambient temperature and humidified with saturated air or steam.

[0045] After the humidification, the extrudate is ion exchanged with 0.5 to 1 N ammonium nitrate solution. The ammonium nitrate solution ion exchange is repeated. The ammonium nitrate exchanged extrudate is then washed with deionized water to remove residual nitrate prior to calcination in air. After washing the wet extrudate is dried. The exchanged and dried extrudate is next calcined in a nitrogen/air mixture to a temperature 1000°F (538°C). Afterwards, the calcined extrudate is cooled to room temperature. The 80% MCM-49, 20% Al₂O₃ extrudate was incipient wetness impregnated with a palladium (II) chloride solution (target: 0.30% Pd) 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 ambient to 538°C at 1°C/min and hold for 3 hours.

Example 2: Hydroalkylation of Toluene

[0046] The catalyst of Example 1 was then tested in the hydroalkylation of a toluene feed using the reactor and process described below.

15 [0047] The reactor comprised a stainless steel tube having an outside diameter of: 3/8 inch (0.95 cm), a length of 20.5 inch (52 cm) and a wall thickness of 0.35 inch (0.9 cm). A piece of stainless steel tubing having a length of 8¾ inch (22 cm) and an outside diameter of 3/8 inch (0.95 cm) and a similar length of ¼ inch (0.6 cm) tubing were used in the bottom of the reactor (one inside of the other) as a spacer to position and support the catalyst in the isothermal zone of the furnace. A ¼ inch (0.6 cm) plug of glass wool was placed on top of the spacer to keep the catalyst in place. A 1/8 inch (0.3 cm) stainless steel thermo-well was placed in the catalyst bed to monitor temperature throughout the catalyst bed using a movable thermocouple.

[0048] 1 gm of the catalyst was sized to 20/40 sieve mesh or cut to 1:1 length to diameter ratio, dispersed with quartz chips (20/40 mesh) then loaded into the reactor from the top to a volume of 5.5 cc. The catalyst bed typically was 15 cm. in length. 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).

[0049] The catalyst was pre-conditioned in situ by heating from 25°C to 240°C with H₂ flow at 100 cc/min and holding for 12 hours. A 500 cc ISCO syringe pump was used to introduce 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). GC analyses were taken to verify feed composition. The feed was then pumped through the catalyst bed held at the reaction
5 temperature of 120°C to 180°C at a WHSV of 2 and a pressure of 15-200 psig (204-1480 kPa). 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 about 10°C. Material balances were taken at 12 to 24 hrs intervals. Samples were taken and diluted with 50% ethanol for analysis. An Agilent™ 6890 gas
10 chromatograph with FID detector was used for the analysis. The non-condensable gas products were routed to an on-line Hewlett Packard™ 5890 GC.

[0050] The major components of the hydroalkylation reaction effluent were toluene (66 wt%), (methylcyclohexyl)toluene (24 wt%), methylcyclohexane (9 wt%) and dialkylate (0.5 wt%).

15 **Example 3: Preparation of 1%Pt/0.15%Sn/SiO₂ Dehydrogenation Catalyst**

[0051] A 1%Pt/0.15%Sn/SiO₂ dehydrogenation catalyst was prepared by incipient wetness impregnation. A 1/20" quadralobe silica extrudate was initially impregnated with an aqueous solution of tin chloride and then dried in air at 121°C. The resultant tin-containing extrudates were then impregnated with an aqueous solution of tetraammine Pt
20 nitrate and again dried in air at 121°C. The resultant product was calcined in air at 350°C for 3 hours before being used in subsequent catalyst testing.

Example 4: Activation and Use of Dehydrogenation Catalyst of Example 3

[0052] The catalyst of Example 3 was used to dehydrogenate the hydroalkylation reaction effluent of Example 2 using the reactor and process described below.

25 [0053] The catalyst extrudate was crushed to 20/40 mesh and loaded into 9 mm diameter quartz tube reactors in quantities ranging from 0.25-1g (to vary the corresponding weight based space velocity) after being diluted up to 4g in crushed quartz. A quartz wool plug was used at the top and bottom of the catalyst bed to keep catalyst in place. 2 sets of 4 parallel reactors were placed in heated furnaces to control isothermal reaction temperature. Each
30 reactor contained an internal thermocouple in the catalyst bed in a 1/8" thermowell. The reactors were topped off with the same quartz chips.

[0054] The catalyst in all reactors was activated *in situ* by the following procedure. The reactor was purged with H₂ for 30 minutes. Then the temperature was ramped at 9°F (5°C)/hr. to 248°F (120°C) and then held at 248°F (120°C) for 1 hr to dry the catalyst. Hydrogen flow

was set to 56 cc/min, the pressure was adjusted to 50 psig (446 kPa-a) and the temperature was ramped at 9°F (5°C)/hr. to 842°F (450°C). The temperature was held at 842°F (450°C) for 12 hours. At the end of 12 hrs, the temperature was ramped down at 9°F (5°C)/hr. to the desired dehydrogenation temperature. The pressure was then increased to 100 psig (791 kPa-a). Feed was introduced at these conditions via ISCO pumps.

[0055] The feed was pumped through a vaporizer before being mixed in-line with H₂ at a 2:1 to 4:1 molar ratio of H₂ to liquid feed. The feed was then pumped through the catalyst bed held at the reaction temperature of between 350°C and 450°C. WHSV was varied between 2 and 16. The products exiting the reactor were condensed and collected in intervals (approximately one sample per day per reactor) and analyzed by GC. The results are shown in Figures 1 and 2. In particular, it will be seen that, by increasing the H₂:hydrocarbon molar feed ratio from 2 to 4, the catalyst activity (measured by MCHT conversion) remained higher over a longer period of time (Figure 1). Specifically, at a temperature of 400°C and 8 WHSV, MCHT conversion at 730 hours on stream is greater than 80% in the case of H₂:hydrocarbon =4. In the case of H₂:hydrocarbon=2, the conversion is less than 70%. Further, at WHSV=16, the conversion of MCHT declines more rapidly at higher temperatures (Figure 2).

Example 5: Alternative Activation Process for Dehydrogenation Catalyst of Example 3

[0056] The dehydrogenation process of Example 4 was repeated but with the catalyst being initially activated *in situ* by heating from room temperature to 430°C with H₂ flow at 100 cc/min, at a temperature ramping rate of 2°C/min and 100 psig (791 kPa-a) pressure.

[0057] The results of the dehydrogenation processes of Examples 4 and 5 at a temperature of 430°C, WHSV of 2 and H₂/HC of 2:1 (molar) are compared in Figure 3. In the case of the process of Example 4, the amount of dialkylate in the feed was varied during the test from 0.21 wt% for the first 550 hours, to 0.722 wt% for the next 450 hours, to 0.415 wt% for the next 175 hours, and to 0.843 wt% for the final 325 hours (for a total of about 1500 hours from the beginning of the test). In the case of the process of Example 5, the amount of dialkylate in the feed was maintained at 0.21 wt% throughout the duration of the test. It will be seen that, with the activation procedure of Example 4, it was possible to run the reaction for more than 1500 hrs with only limited catalyst deactivation. In contrast, the catalyst produced by the procedure of Example 5 deactivated more rapidly, even though the dialkylate content of the feed was always at or below the level in Example 4.

[0058] 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. All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not
5 inconsistent with this text. Likewise, the term "comprising" is considered synonymous with the term "including" for purposes of Australian law and whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is"
10 preceding the recitation of the composition, element, or elements and vice versa.

CLAIMS

We claim:

1. A process for dehydrogenating cyclohexylbenzene and/or alkyl-substituted cyclohexylbenzene compounds, the process comprising:
 - 5 (a) providing a dehydrogenation catalyst comprising at least one Group 10 metal compound on a support;
 - (b) heating the dehydrogenation catalyst in the presence of hydrogen from a first temperature from 0°C to 200°C to a second, higher temperature from 60°C to 500°C at a ramp rate no more than 100°C/hour;
 - 10 (c) contacting the dehydrogenation catalyst with hydrogen at the second temperature for a time from 3 to 300 hours to produce an activated dehydrogenation catalyst; and
 - (d) contacting a feed comprising cyclohexylbenzene and/or an alkyl-substituted cyclohexylbenzene compound with hydrogen in the presence of the activated
15 dehydrogenation catalyst under conditions effective to produce a dehydrogenation reaction product comprising biphenyl and/or an alkyl-substituted biphenyl compound.
2. The process of claim 1, wherein the at least one Group 10 metal comprises platinum.
3. The process of claim 1, wherein the dehydrogenation catalyst comprises from 0.1 to 5% wt% of elemental platinum.
- 20 4. The process of claim 1, wherein the dehydrogenation catalyst further comprises a tin compound.
5. The process of claim 1, wherein the dehydrogenation catalyst comprises from 0.1 to 5 wt% of elemental tin.
6. The process of claim 1 and further comprising:
 - 25 (e) treating a support with a solution containing a Group 10 metal compound in a solvent; and
 - (f) removing the solvent from the treated support to produce the dehydrogenation catalyst on a support provided in (a).
7. The process of claim 1, wherein the temperature ramp during the heating (b) is from
30 0.5°C/hour to 100°C/hour.
8. The process of claim 1, wherein the temperature ramp during the heating (b) is from 0.5°C/hour to 50°C/hour.
9. The process of claim 1, wherein the temperature ramp during the heating (b) is from 1°C/hour to 20°C/hour.

10. The process of claim 1, wherein hydrogen is supplied to the dehydrogenation catalyst at least during the contacting (c) at a rate of 10 to 300 sccm/g of catalyst.
11. The process of claim 1, wherein the conditions in the contacting (d) include a
5 hydrogen to hydrocarbon molar ratio in excess of 2.
12. The process of claim 1, wherein the conditions in the contacting (d) include a temperature from 200°C to 500°C and a pressure from 100 kPa to 1600 kPa-a.
13. The process of claim 1, wherein the feed comprises less than 0.1 wt% of dicyclohexylbenzene compounds.
- 10 14. The process of claim 1, wherein the feed comprises cyclohexylbenzene produced by the hydroalkylation of benzene.
15. The process of claim 1, wherein the feed comprises (methylcyclohexyl)toluene produced by the hydroalkylation of toluene.
16. The process of claim 1, wherein the feed comprises dimethylcyclohexylxylenes from
15 the hydroalkylation of xylenes.
17. The process of claim 1, wherein the feed comprises methylcyclohexylbenzene and/or cyclohexyltoluene produced from the hydroalkylation of toluene and benzene or the transalkylation of cyclohexylbenzene with toluene.
18. The process of claim 1, wherein the reactor feed also contains up to 90 wt% benzene
20 or cyclohexane.
19. The process of claim 1, wherein the reactor feed also contains up to 90 wt% alkylated benzene or alkylated cyclohexane.
20. The process of claim 1, wherein the reactor feed also contains up to 90 wt% toluene and/or methylcyclohexane.
- 25 21. The process of claim 1, wherein the first temperature is at least 100°C higher than the second temperature in (b).
22. The process of claim 1, wherein the support is selected from the group consisting of alumina, silica, silica-alumina, titania, calcium oxide, strontium oxide, barium oxide, magnesium oxide, carbon, zirconia, diatomaceous earth, lanthanide oxides including cerium
30 oxide, lanthanum oxide, neodymium oxide, yttrium oxide and praeodymium oxide, oxides of chromium, thorium, uranium, niobium and tantalum, tin oxide, zinc oxide, and aluminum phosphate.

23. The process of claim 4, wherein the tin compound comprises tin chloride or tin tartrate.
24. The process of claim 1, wherein the conditions in the contacting (d) include a hydrogen to hydrocarbon molar ratio of at least 4.
- 5 25. The process of claim 1, wherein the feed of (d) comprises less than 0.1 wt% of dicyclohexylbenzene.

1/2

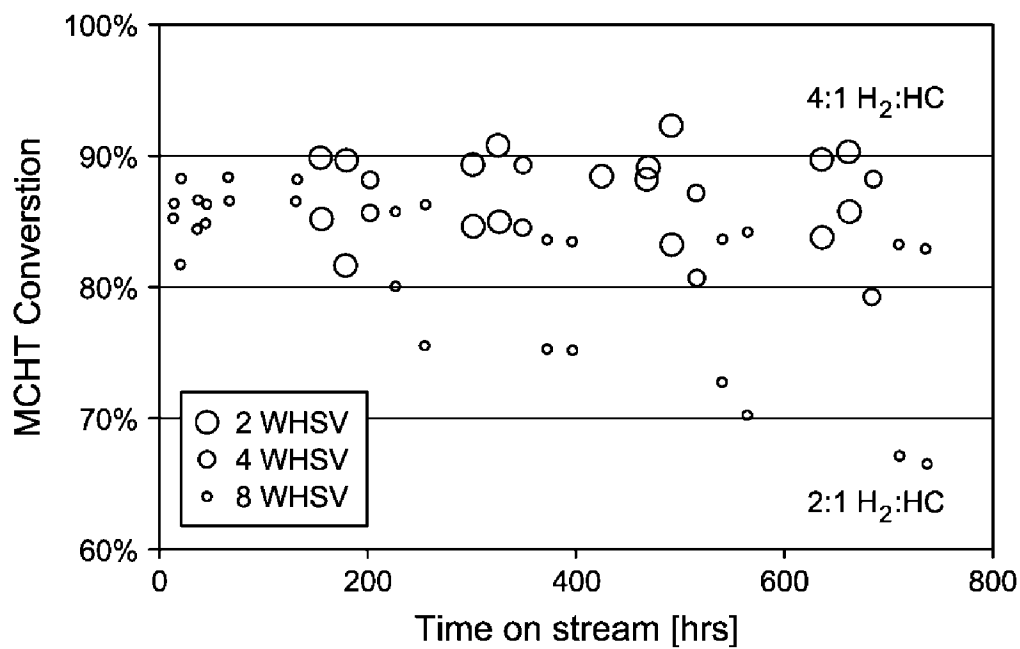


FIG. 1

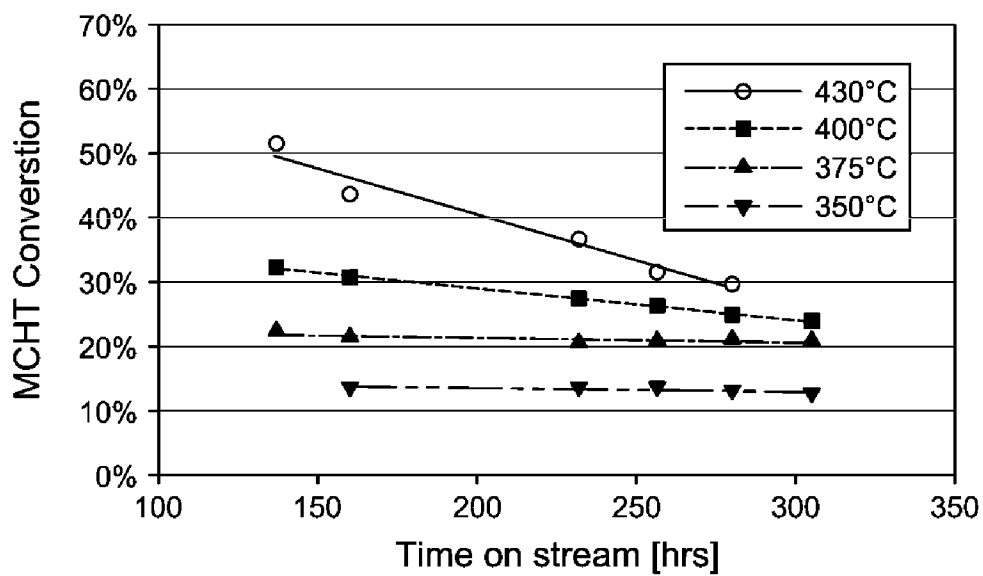


FIG. 2

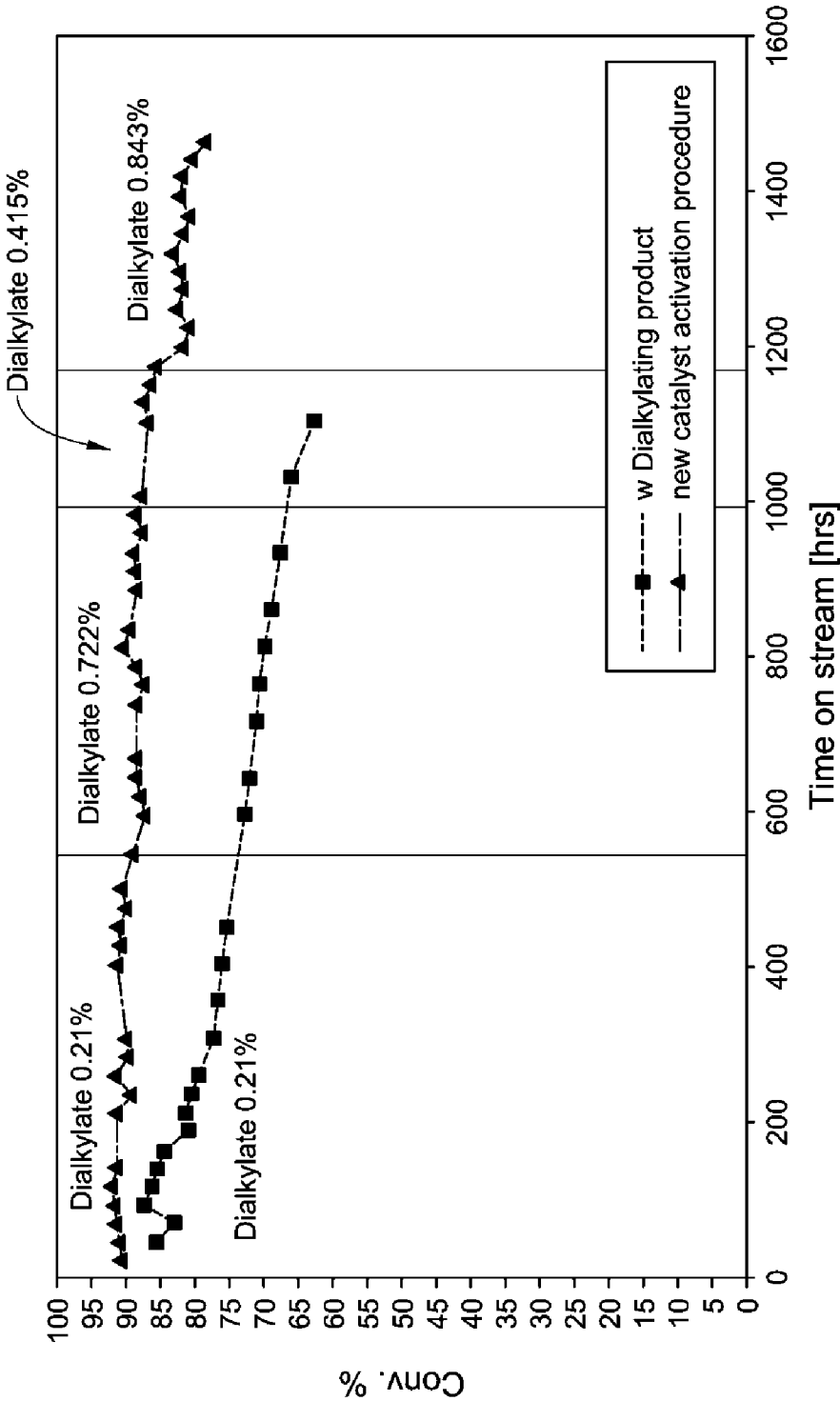


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/054729**A. CLASSIFICATION OF SUBJECT MATTER****B01J 23/42(2006.01)i, B01J 23/14(2006.01)i, B01J 32/00(2006.01)i, C07C 2/66(2006.01)i, C07C 13/28(2006.01)i**

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 23/42; C07C 5/38; C07C 67/08; B01J 23/62; C07C 37/06; C07C 2/66; C07C 2/64; C07C 2/74; B01J 23/22; B01J 23/14; B01J 32/00; C07C 13/28

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: cyclohexylbenzene, methylbisphenyl compound, dehydrogenation, catalyst, activation, Pt-Sn/SiO₂**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2014-0275609 A1 (EXXONMOBIL CHEMICAL PATENTS INC.) 18 September 2014 See abstract; paragraphs [0031], [0052], [0073]–[0075]; and claims 1–14.	1–25
A	US 2014-0066663 A1 (DAKKA, JIHAD M. et al.) 06 March 2014 See abstract; paragraphs [0115]–[0118]; and claim 25.	1–25
A	US 7579511 B1 (DAKKA, JIHAD M. et al.) 25 August 2009 See abstract; column 11, lines 5–46; claims 1, 4; and figure 1.	1–25
A	US 4218572 A (DOLHYJ, SERGE R. et al.) 19 August 1980 See abstract; and claims 1–21.	1–25
A	DEPBOYLU, CAN OKAN, "An investigation of catalyst preparation conditions and promoter loading (Sn) effects on activity and selectivity of Pt catalysts in citral hydrogenation," Izmir Institute of Technology, Master Thesis, 2010, internal pages 1–59 See pages 38–41, 45, 46; and figures 26, 33.	1–25



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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Information on patent family members

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