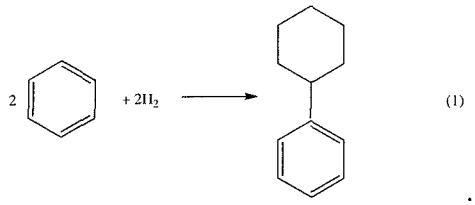
embodiments, the support comprises an inorganic oxide such as one or more of silicon dioxide, titanium dioxide, and zirconium dioxide. The support may or may not comprise a binder. Impurities that can be present in the catalyst support are, for example, sodium salts such as sodium silicate which can be present from anywhere from 0.01 wt% to 2 wt%. Suitable silica supports are described in, for example, PCT Pub. No. WO/2007084440 A1 filed on January 12, 2007, and entitled "Silica Carriers" ~~and is hereby incorporated by reference for this purpose~~.

[0026] It will be understood that the metal selected from Group 14 and/or the metal selected from Groups 6 to 10 of the Periodic Table of Elements may not be purely the elemental metal, but could, for example, be at least partly in another form, such as a salt, oxide, chloride, hydride, sulfide, carbonate, etc. For purposes of this application, the wt% of metal in the catalyst composition is calculated based upon the amount of metal used to form the component in the catalyst composition. Moreover, for purposes of determining wt%s of various components of the dehydrogenation catalyst, only that portion of the support that supports the Group 14 metal and/or the Group 6-10 metal is considered. For example, a catalyst composition made with 1.9 grams of tin chloride salt (1 gram of tin) and 22.29 grams of tetraammine platinum hydroxide solution (4.486 wt% Pt) that is supported on 98 grams of silicon dioxide contains 1 wt% of tin and 1 wt% Pt, based upon total weight of the catalyst composition.

[0027] The dehydrogenation catalyst is typically prepared by sequentially or simultaneously treating the support, such as by impregnation, with one or more liquid compositions comprising the Group 6-10 metal or a precursor thereof, the Group 14 metal or a precursor thereof and/or the optional inorganic base component or a precursor in a liquid carrier, such as water. An organic dispersant may be added to each liquid carrier to assist in uniform application of the metal component(s) to the support. Suitable organic dispersants include amino alcohols and amino acids, such as arginine. Generally, the organic dispersant is present in the liquid composition in an amount between 1 wt% and 20 wt% of the liquid composition.

[0028] In one preferred embodiment, the catalyst is prepared by sequential impregnation with the Group 14 metal component being applied to the support before the Group 6-10 metal component.

[0029] After treatment with the liquid composition, the support is heated in one or more stages, generally at a temperature of 100°C to 700°C for a time of 0.5 to 50 hours, to effect one or more of: (a) removal of the liquid carrier; (b) conversion of a metal component to a catalytically active form; and (c) decompose the organic dispersant. The heating may be



[0037] 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 kPa and 7,000 kPa, such as between 500 kPa and 5,000 kPa. Suitable values for the molar ratio of hydrogen to benzene are between 0.15:1 and 15:1, such as between 0.4:1 and 4:1 for example, between 0.4 and 0.9:1.

[0038] The catalyst employed in the hydroalkylation reaction is generally a bifunctional catalyst comprising a molecular sieve of the MCM-22 family and a hydrogenation metal. 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.

[0039] 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

accomplished by introducing an oxygen-containing gas, such as air, into a liquid phase containing the cyclohexylbenzene. Unlike the Hock process, atmospheric air oxidation of cyclohexylbenzene, in the absence of a catalyst, is very slow and hence the oxidation is normally conducted in the presence of a catalyst.

[0052] Suitable catalysts for the cyclohexylbenzene oxidation step are the N-hydroxy substituted cyclic imides described in U.S. Patent No. 6,720,462 ~~and incorporated herein by reference~~, such as N-hydroxyphthalimide, 4-amino-N-hydroxyphthalimide, 3-amino-N-hydroxyphthalimide, tetrabromo-N-hydroxyphthalimide, tetrachloro-N-hydroxyphthalimide, N-hydroxyhetimide, N-hydroxyhimimide, N-hydroxytrimellitimide, N-hydroxybenzene-1,2,4-tricarboximide, N,N'-dihydroxy(pyromellitic diimide), N,N'-dihydroxy(benzophenone-3,3',4,4'-tetracarboxylic diimide), N-hydroxymaleimide, pyridine-2,3-dicarboximide, N-hydroxysuccinimide, N-hydroxy(tartaric imide), N-hydroxy-5-norbornene-2,3-dicarboximide, exo-N-hydroxy-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide, N-hydroxy-cis-cyclohexane-1,2-dicarboximide, N-hydroxy-cis-4-cyclohexene-1,2 dicarboximide, N-hydroxynaphthalimide sodium salt or N-hydroxy-o-benzenedisulphonimide. Preferably, the catalyst is N-hydroxyphthalimide. Another suitable catalyst is N,N',N"-thihydroxyisocyanuric acid.

[0053] These materials can be used either alone or in the presence of a free radical initiator and can be used as liquid-phase, homogeneous catalysts or can be supported on a solid carrier to provide a heterogeneous catalyst. Typically, the N-hydroxy substituted cyclic imide or the N,N',N"-trihydroxyisocyanuric acid is employed in an amount between 0.0001 wt% to 15 wt%, such as between 0.001 wt% to 5 wt%, of the cyclohexylbenzene.

[0054] Suitable conditions for the oxidation step include a temperature between 70°C and 200°C, such as 90°C to 130°C, and a pressure of 50 kPa to10,000 kPa. Any oxygen-containing gas, preferably air, can be used as the oxidizing medium. The reaction can take place in batch reactors or continuous flow reactors. A basic buffering agent may be added to react with acidic by-products that may form during the oxidation. In addition, an aqueous phase may be introduced, which can help dissolve basic compounds, such as sodium carbonate.

[0055] The another reactive step in the conversion of the cyclohexylbenzene into phenol and cyclohexanone involves cleavage of the cyclohexylbenzene hydroperoxide, which is conveniently effected by contacting the hydroperoxide with a catalyst in the liquid phase at a temperature of 20°C to 150°C, such as 40°C to 120°C, a pressure of 50 kPa to 2,500 kPa, such as 100 kPa to 1000 kPa. The cyclohexylbenzene hydroperoxide is preferably diluted in an

organic solvent inert to the cleavage reaction, such as methyl ethyl ketone, cyclohexanone, phenol or cyclohexylbenzene, to assist in heat removal. The cleavage reaction is conveniently conducted in a catalytic distillation unit.

[0056] The catalyst employed in the cleavage step can be a homogeneous catalyst or a heterogeneous catalyst.

[0057] Suitable homogeneous cleavage catalysts include sulfuric acid, perchloric acid, phosphoric acid, hydrochloric acid, and p-toluenesulfonic acid. Ferric chloride, boron trifluoride, sulfur dioxide, and sulfur trioxide are also effective homogeneous cleavage catalysts. The preferred homogeneous cleavage catalyst is sulfuric acid, with preferred concentrations in the range of 0.05 wt% to 0.5 wt%. For a homogeneous acid catalyst, a neutralization step preferably follows the cleavage step. Such a neutralization step typically involves contact with a basic component, with subsequent decanting of a salt-enriched aqueous phase.

[0058] A suitable heterogeneous catalyst for use in the cleavage of cyclohexylbenzene hydroperoxide includes a smectite clay, such as an acidic montmorillonite silica-alumina clay, as described in U.S. Patent No. 4,870,217~~, the entire disclosure of which is incorporated herein by reference~~.

[0059] The effluent from the cleavage reaction comprises phenol and cyclohexanone in substantially equimolar amounts and, depending on demand, the cyclohexanone can be sold or can be dehydrogenated into additional phenol. Any suitable dehydrogenation catalyst can be used in this reaction, such as the dehydrogenation catalyst or a variation of the catalyst described herein. Suitable conditions for the dehydrogenation step comprise a temperature of 250°C to 500°C and a pressure of 0.01 atm to 20 atm (1 kPa to 2030 kPa), such as a temperature of 300°C to 450°C and a pressure of 1 atm to 3 atm (100 kPa to 300 kPa).

[0060] The invention will now be more particularly described with reference to the following non-limiting Examples and the accompanying drawings.

Example 1: Dehydrogenation of cyclohexane

[0061] A first dehydrogenation catalyst comprising 1 wt% platinum and 0.15 wt% tin on a silicon oxide support and a second dehydrogenation catalyst (comparative) comprising 1 wt% platinum and 1 wt% potassium on a silicon oxide support were crushed to 60/100 mesh and loaded into ½" (1.27 cm) outer diameter (OD) tubular downflow reactors. The catalysts were then separately contacted with a composition comprising 89 wt% benzene, 10 wt% cyclohexane and 1 wt% methylcyclopentane under dehydrogenation conditions of 480°C, 0.689 MPa, 10 hr^{-1} weight hourly space velocity (WHSV), and a molar ratio of hydrogen to

hydrocarbon (H_2/HC) of 4. As illustrated in Figure 1, the Pt/Sn/SiO_2 catalyst achieved significantly higher cyclohexane conversion and selectivity than the Pt/K/SiO_2 catalyst.

[0062] 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 without departing from the spirit and scope of the invention. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

PCT CLAIMS

1. A dehydrogenation process comprising:

contacting a composition comprising at least 50 wt% of an aromatic hydrocarbon and at least 0.1 wt% of a saturated six-membered cyclic hydrocarbon, the wt%s based upon total weight of the composition, with a dehydrogenation catalyst to produce the aromatic hydrocarbon, the dehydrogenation catalyst comprising metals consisting essentially of:

(i) 0.05 to 5 wt% of ~~a metal selected from Group 14 of the Periodic Table of Elements~~ tin; and (ii) 0.1 to 10 wt% of a metal selected from ~~Groups 6 to~~ Group 10 of the Periodic Table of Elements, the wt%s based upon total weight of the dehydrogenation catalyst.

2. The process of claim 1, wherein the aromatic hydrocarbon is benzene.

3. The process of claim 1 or claim 2, wherein the composition comprises at least 1 wt% of the saturated six-membered cyclic hydrocarbon, the wt% based upon total weight of the composition.

4. The process of any one of the preceding claims, wherein the saturated six-membered cyclic hydrocarbon is cyclohexane.

5. The process of claim 4, wherein the dehydrogenation catalyst converts at least 70% of the cyclohexane to benzene.

6. The process of any one of the preceding claims, wherein the dehydrogenation catalyst comprises 0.1 to 0.5 wt% of tin~~the metal selected from Group 14 of the Periodic Table of Elements~~, based upon total weight of the dehydrogenation catalyst.

7. The process of any one of the preceding claims, wherein the dehydrogenation catalyst comprises 0.15 to 0.3 wt% of ~~the metal selected from Group 14 of the Periodic Table of Elements~~ tin, based upon total weight of the dehydrogenation catalyst.

8. The process of any one of the preceding claims, wherein the dehydrogenation catalyst comprises 0.5 to 5 wt% of the metal selected from ~~Groups 6 to~~ Group 10 of the Periodic Table of Elements, based upon total weight of the dehydrogenation catalyst.

~~9. The process of any one of the preceding claims, wherein the metal selected from Group 14 of the Periodic Table of Elements is tin.~~

~~10.~~9. The process of any one of the preceding claims, wherein the metal selected from ~~Groups 6 to~~ Group 10 of the Periodic Table of Elements is platinum or palladium.

~~11.~~10. The process of any one of the preceding claims, wherein the dehydrogenation process is conducted under dehydrogenation conditions comprising a temperature between 200°C and 550°C and a pressure between 100 kPa and 7,000 kPa.

~~12.~~11. The process of any one of the preceding claims, wherein the composition further comprises at least 0.01 wt% methylcyclopentane, based upon total weight of the composition.

~~13.~~12. The process of any one of the preceding claims, wherein dehydrogenation catalyst comprises a support containing one or more of silica, alumina, a silicate, an aluminosilicate, zirconia or carbon.

~~14.~~13. The process of any one of the preceding claims, wherein the dehydrogenation catalyst comprises a support containing an inorganic oxide selected from silicon dioxide, titanium dioxide and zirconium oxide.

~~15.~~14. A dehydrogenation process comprising:

(a) providing a composition comprising at least 0.1 wt% of a saturated six-membered cyclic hydrocarbon and at 0.05 wt% of a saturated five-membered ~~ring compound~~ cyclic hydrocarbon; and

(b) producing a dehydrogenation reaction product by contacting at least a portion of the composition with a dehydrogenation catalyst under conditions effective to convert: (i) at least a portion of the at least one saturated six-membered cyclic hydrocarbon to benzene; and (ii) at least a portion of the at least one five-membered ~~ring compound~~ cyclic hydrocarbon to at least one paraffin,

wherein the dehydrogenation catalyst comprises metals consisting essentially of: (i) 0.05 wt% to 0.5 wt% of ~~a metal selected from Group 14 of the Periodic Table of Elements~~ tin;

and (ii) 0.1 wt% to 2 wt% of a metal selected from ~~Groups 6 to~~ Group 10 of the Periodic Table of Elements, the wt%s based upon total weight of the dehydrogenation catalyst.

~~16.~~15. The process of claim ~~15~~ 14, wherein the saturated six-membered cyclic hydrocarbon is cyclohexane.

~~17.~~16. The process of claim ~~15~~ 14 or claim ~~16~~ 15, wherein the saturated five-membered ~~ring compound~~cyclic hydrocarbon is methylcyclopentane.

~~18. The process of any one of claims 15-17, wherein the metal selected from Group 14 of the Periodic Table of Elements is tin.~~

~~19.~~17. The process of any one of claims ~~15-18~~ 14-16, wherein the metal selected from ~~Groups 6 to~~ Group 10 of the Periodic Table of Elements is platinum or palladium.

~~20.~~18. The dehydrogenation process of any one of claims ~~15-19~~ 14-17, wherein the dehydrogenation catalyst comprises a support, and the dehydrogenation catalyst is produced by a method comprising:

(i) treating the support with ~~the Group 14 metal~~ tin to form a treated support;

(ii) calcining the treated support at a temperature of 100°C to 700°C;

(iii) impregnating the support with the ~~Group 6 to~~ Group 10 metal to form an impregnated support; and

(iv) calcining the impregnated support at a temperature of 100°C to 700°C,

wherein the impregnating step (iii) is effected prior to or at the same time as the treating step (i).

~~21.~~19. The process of claim ~~20~~ 18, wherein the impregnating step (iii) is effected after the calcining step (ii).

~~22.~~20. The process of claim ~~20~~ 18 or claim ~~21~~ 19, wherein the calcining step (iv) is conducted in an oxygen-containing atmosphere at a temperature of 200°C to 500°C for a time of 1 to 10 hours.

~~23.~~21. The process of any one of claims ~~15-22~~ 14-20, wherein the at least one saturated six-membered cyclic hydrocarbon is cyclohexane, which is present in an amount of at least 5 wt%, based upon total weight of the composition.

~~24.~~22. The process of any one of claims ~~15-23~~ 14-21, wherein the at least one saturated five-membered ~~ring-compound~~cyclic hydrocarbon is methylcyclopentane, which is present in an amount of at least 0.1 wt%, based upon total weight of the composition.

~~25.~~23. A process for producing cyclohexylbenzene, the process comprising:

(a) contacting benzene and hydrogen in the presence of a hydroalkylation catalyst under hydroalkylation conditions effective to form a hydroalkylation reaction product comprising cyclohexylbenzene, cyclohexane, methylcyclopentane, and benzene;

(b) separating at least a portion of the hydroalkylation reaction product into (i) a first composition that is rich in at least one of benzene, cyclohexane, and methylcyclopentane; and (ii) a second composition that is rich in cyclohexylbenzene;

(c) contacting at least a portion of the first composition with a dehydrogenation catalyst under conditions effective to convert at least a portion of the cyclohexane to benzene,

wherein the dehydrogenation catalyst comprises metals consisting essentially of: (i) 0.05 to 0.5 wt% of tin ~~a metal selected from Group 14 of the Periodic Table of Elements~~; and (ii) 0.1 to 2 wt% of a metal selected from ~~Groups 6 to~~ Group 10 of the Periodic Table of Elements, the wt%s based upon total weight of the dehydrogenation catalyst; and

(d) recycling at least a portion of the benzene formed in step (c) to the contacting step (a).