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**PREPARATION OF ARYLNAPHTHENES FROM AROMATIC HYDROCARBONS**

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The present invention relates to the preparation of aryl-naphthenes and/or alkyl substituted aryl-naphthenes from aromatic hydrocarbons and/or alkyl substituted aromatic hydrocarbons.

Naphthenes are defined herein as hydrocarbons the molecule of which contains at least one saturated hydrocarbon ring.

It is known to prepare naphthenes such as cyclohexane and decahydronaphthalene by the hydrogenation of aromatic hydrocarbons such as benzene and naphthalene with the aid of hydrogen catalysts. This procedure has the disadvantage that the catalysts employed are relatively expensive.

It has also been proposed to obtain aromatic hydrocarbons by heating ethylene alone or admixed with other hydrocarbons, e.g. propene, at superatmospheric pressure in the presence of a heteropolyacid.

The term heteropolyacid is defined herein as an acid belonging to the group of complex acids composed of more than one metallic oxide or metalloid oxide.

It is an object of the present invention to develop an improved procedure for converting aromatic hydrocarbons, including alkyl substituted aromatic hydrocarbons, into aryl-naphthenes (including alkaryl-naphthenes).

Another object is to reduce the amount of hydrogenation catalyst required in converting aromatic hydrocarbons (including alkyl substituted aromatic hydrocarbons) into aryl-naphthenes (including alkaryl-naphthenes).

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained and aryl-naphthenes and/or alkyl substituted aryl-naphthenes can be obtained from aromatic hydrocarbons (including alkyl aromatic hydrocarbons) if the aromatic hydrocarbon in the liquid phase is hydrogenated with hydrogen at a hydrogen pressure below 100 atmospheres and at a temperature not over 250° C. while using a mixture of a hydrogenation catalyst and a heteropolyacid as cocatalysts. The hydrogen pressure can be as low as 5 atmospheres and the temperature can be as low as 125° C.

The invention can be employed for example to prepare phenylcyclohexane from benzene tolyl methylcyclohexane from toluene dimethylphenyl dimethyl cyclohexane from xylene (any of the isomers o-xylene, p-xylene or m-xylene or a mixture thereof can be employed) butylphenyl butylcyclohexane from n-butylbenzene naphthyl decahydronaphthalene from naphthalene decylphenyl decylcyclohexane from decylbenzene phenyl decahydronaphthalene from a mixture of benzene and naphthalene (e.g. a 1:1 molar mixture) methyl-naphthyl methyl-decahydronaphthalene from methyl naphthalene methylphenyl decahydronaphthalene from a mixture of toluene and xylene (e.g. a 1:2 molar mixture).

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It will be realized that in some instances the reaction will result in the formation of position isomers. When this is so there is no need to separate the isomers formed.

Suitable heteropolyacid catalysts according to the invention include silicotungstic acid, borotungstic acid, phosphotungstic acid, phosphomolybdic acid, boronmolybdic acid, silicomolybdic acid, phosphotungstomolybdic acid, arsenomolybdic acid, antimonotungstic acid and phosphovanadic acid.

Representative examples of the hydrogenation catalysts are metals such as nickel, cobalt, iron, platinum, palladium, iridium, osmium, rhodium, ruthenium and tungsten, oxides such as chromium oxide e.g. chromic oxide, molybdenum oxide and tungsten oxide and selenium oxide as well as sulfides such as molybdenum sulfide, nickel sulfide, tungsten sulfide and iron sulfide.

The amount of hydrogenation catalyst in the catalyst combination can be varied. One of the advantages of the invention is that it can be quite small, e.g. 0.1-2.5% of the hydrogenation catalyst by weight of the heteropolyacid is sufficient to give good results in the reaction. It is possible to employ larger amounts of the hydrogenation catalyst, e.g. 3, 5, 15 or 20% by weight of the heteropolyacid. In fact there can be used as much as 35% of the hydrogenation catalyst based on the weight of the heteropolyacid. However, as previously stated, one of the advantages of the present invention is that only very small amounts of the costly hydrogenation catalyst suffice to obtain satisfactory yields of the low boiling aryl-naphthenes.

It is frequently desirable, although not essential, to apply the catalyst combination on a carrier. In such case the carrier can be 40 to 90% by weight based on the total weight of the hydrogenation catalyst, heteropolyacid and carrier.

Examples of suitable carriers include thorium oxide, aluminum oxide, magnesium oxide, zirconium oxide, silicon dioxide, silicic acid gel, diatomaceous earth, kieselguhr, pumice and carbon. These can also be used as the carrier substances which are suitable for promoting the cracking of hydrocarbons to liquid and/or gaseous products. Examples of such cracking catalysts include acid metal silicates composed of silicon dioxide and metal oxides such as aluminum oxide, calcium oxide, zirconium oxide, magnesium oxide, rare earth metal oxides, e.g. hafnium oxide and cerium oxide, and zinc oxide. Other inorganic oxides such as barium oxide can also be present. Likewise there can be used acid clay and cracking catalysts substantially consisting of silicon dioxide.

The cocatalysts can be employed in an amount of 1/2 to 10% based on the weight of the aromatic hydrocarbon reactant.

The combination of the hydrogenation catalyst and heteropolyacid can be obtained in several ways. Thus an intimate mixture of the two materials can be made simply by mixing the preformed materials. An alternative procedure is to prepare the hydrogenation catalyst in the presence of the heteropolyacid. One way of carrying out the latter procedure is to distribute a heteropolyacid in a solution of a compound of the metal which is to serve as the hydrogen catalyst and to complete the preparation of the hydrogenation catalysts after removal of the solvent, e.g. by reducing the compound of the metal to the free metal.

As has been previously set forth the present process can be carried out under conventional temperature and pressure conditions for a hydrogen treatment. Thus the temperature should not be above 250° C. and the hydrogen pressure should be below 100 atmospheres. The temperature and pressure are also selected so that the reaction takes place in the liquid phase.

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The hydrogen employed need not be pure but it can be diluted with inert gases such as nitrogen, argon and saturated hydrocarbons such as methane, ethane, propane, butane and tetramethylmethane. Saturated hydrocarbons can also be added in the liquid phase as diluents. Illustrative of such materials are cyclohexane, decahydronaphthalene, n-heptane, n-decane, 2-methylhexane.

Unless otherwise indicated all parts and percentages are by weight.

#### Example 1

The catalyst employed consisted of 0.7% platinum, 20% silicotungstic acid and 79.3% of powdered silicic acid gel. The catalyst was prepared by impregnating silicic acid gel with an aqueous solution of silicotungstic acid and chloroplatinic acid, evaporating the water and finally reducing the dry product with hydrogen.

There were distributed 35 grams of the catalyst mixture in 700 cc. of benzene in a 2 liter autoclave provided with a stirrer. Then hydrogen was introduced into the autoclave and the reaction mixture was heated at 150° C. for 4 hours while stirring. The pressure was kept at 10 atmospheres. After cooling to room temperature, the liquid reaction product was separated from the catalyst and fractionally distilled to give a product analyzing 16.3% phenylcyclohexane, 35.4% cyclohexane, 36.0% benzene and 12.3% higher boiling products.

#### Example 2

The procedure of Example 1 was followed except that the temperature was raised to 185–190° C. and the pressure was raised to 30 atmospheres. The product analyzed 25.1% phenylcyclohexane, 12.7% cyclohexane, 57.1% benzene and 5.1% higher boiling products. Thus raising the temperature and pressure while reducing the total amount of conversion of the aromatic hydrocarbon increased the yield of the desired aryl naphthene while reducing the amount of by-products.

#### Example 3

There were distributed 35 grams of a catalyst mixture consisting of 0.2% palladium, 20% silicotungstic acid and 79.8% silicic acid gel in 700 cc. of toluene in the autoclave used in Example 1. Then hydrogen was introduced and the reaction mixture heated at 150° C. for 4 hours while keeping the pressure at 10 atmospheres. After cooling to room temperatures the liquid reaction product was separated from the catalyst and fractionally distilled to give a product analyzing 16.4% tolyl methylcyclohexane, 20.6% methylcyclohexane, 53% toluene and 10% higher boiling products.

#### Example 4

Aluminum oxide was impregnated with an aqueous solution of nickel nitrate and silicotungstic after which the water was evaporated and the dry substance reduced with hydrogen. The catalyst thus obtained was composed of 1% nickel, 10% silicotungstic acid and 89% of aluminum oxide.

700 cc. of benzene were treated with 35 grams of this catalyst at a hydrogen pressure of 30 atmospheres at a temperature of 185–190° C. for 4 hours. The reaction produced analyzed 19.4% phenylcyclohexane, 5.2% cyclohexane, 69.2% benzene and 6.2% higher boiling products.

#### Example 5

The procedure of Example 3 was repeated but the catalyst was replaced by 35 grams of one having an aluminum silicate cracking catalyst (Al<sub>2</sub>O<sub>3</sub> content 13%) as a carrier. The activity of the cracking catalyst was reduced by passing a mixture of 80% by volume of air and 20% by volume of steam over it for 2 hours at 800° C. The catalyst employed for treating the benzene thus contained 1% nickel, 10% silicotungstic acid and 89% of the aluminum silicate. After a reaction time of 8 hours at 185–190° C. and 30 atmospheres of hydrogen the product

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analyzed 30.4% phenylcyclohexane, 10.1% cyclohexane, 26.1% benzene, 27.8% dicyclohexylbenzene and 5.6% higher boiling products (chiefly tricyclohexylbenzene).

What is claimed is:

1. A process for preparing a member of the group consisting of aryl naphthenes and alkaryl naphthenes comprising treating a member of the group consisting of aromatic hydrocarbons and alkyl substituted aromatic hydrocarbons in the liquid phase with hydrogen at a hydrogen pressure of less than 100 atmosphere and at a temperature not over 250° C. while in contact with a catalyst containing (1) a heteropolyacid and (2) a second hydrogenation catalyst.
2. A process according to claim 1 wherein said second hydrogenation catalyst is used in an amount of 0.1 to 35% of the heteropolyacid.
3. A process according to claim 1 wherein a carrier is employed in addition to the catalysts.
4. A process according to claim 3 wherein the carrier is selected from the group consisting of acid metal silicate cracking catalysts, acid clay, silicon dioxide, silicic acid gel, kieselguhr, diatomaceous earth, pumice, carbon and metal oxides.
5. A process according to claim 1 wherein the second hydrogenation catalyst is selected from the group consisting of metals, metal oxides and metal sulfides and the heteropolyacid is selected from the group consisting of silicotungstic acid, borontungstic acid, phosphotungstic acid, phosphomolybdic acid, boronmolybdic acid, silicomolybdic acid, phosphotungstomolybdic acid, arsenomolybdic acid, antimonotungstic acid and phosphovanadic acid.
6. A process for preparing an aryl naphthene comprising treating benzene in the liquid phase with hydrogen at a hydrogen pressure of less than 100 atmospheres and at a temperature not over 250° C. while in contact with a catalyst containing (1) a heteropolyacid and (2) a second hydrogenation catalyst.
7. A process according to claim 6 wherein the second hydrogenation catalyst is a metal and the heteropolyacid is a member of the group consisting of silicotungstic acid, borontungstic acid, phosphotungstic acid, phosphomolybdic acid, boronmolybdic acid, silicomolybdic acid, phosphotungstomolybdic acid, arsenomolybdic acid, antimonotungstic acid and phosphovanadic acid.
8. A process according to claim 6 wherein the catalyst includes a carrier selected from the group consisting of acid metal silicate cracking catalysts, acid clay, silicon dioxide, silicic acid gel, kieselguhr, diatomaceous earth, pumice, carbon and metal oxides.
9. A process according to claim 6 wherein the heteropolyacid is silicotungstic acid and the second hydrogenation catalyst is a metal.
10. A process according to claim 9 wherein the metal is platinum.
11. A process according to claim 9 wherein the metal is palladium.
12. A process for preparing an alkyl substituted aryl naphthene comprising treating a lower alkyl substituted benzene in the liquid phase with hydrogen at a hydrogen pressure of less than 100 atmospheres and at a temperature not over 250° C. while in contact with a catalyst containing (1) a heteropolyacid and (2) a second hydrogenation catalyst.
13. A process according to claim 12 wherein the second hydrogenation catalyst is a metal and the heteropolyacid is a member of the group consisting of silicotungstic acid, borontungstic acid, phosphotungstic acid, phosphomolybdic acid, boronmolybdic acid, silicomolybdic acid, phosphotungstomolybdic acid, arsenomolybdic acid, antimonotungstic acid and phosphovanadic acid.
14. A process according to claim 12 wherein the catalyst includes a carrier selected from the group consisting of acid metal silicate cracking catalysts, acid clay, silicon dioxide, silicic acid gel, kieselguhr, diatomaceous earth, pumice, carbon and metal oxides.

15. A process according to claim 12 wherein the heteropolyacid is silicotungstic acid and the second hydrogenation catalyst is a metal.

16. A process according to claim 15 wherein the metal is platinum.

17. A process according to claim 15 wherein the metal is palladium.

18. A process according to claim 1 wherein there is employed a silicon dioxide carrier with the catalyst.

19. A process according to claim 1 wherein there is employed a silicic acid gel carrier with the catalyst.

20. A process according to claim 1 wherein there is employed an aluminum oxide carrier with the catalyst.

21. A process according to claim 1 wherein there is employed an aluminum silicate cracking catalyst as a carrier for the mixed catalyst.

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