

Description

This invention relates to a catalytic process for cyclizing alkenylbenzenes to the corresponding alkyltetrahydronaphthalenes.

Background of the Invention

Dialkyl-naphthalenes, such as 2,6-dimethylnaphthalenes, are desirable starting materials for oxidation to the corresponding naphthalene dicarboxylic acids. Such acids are monomers that are useful for the preparation of a variety of polymers. For example, 2,6-naphthalene dicarboxylic acid when polymerized with ethylene glycol produces poly(ethylene 2,6-naphthalate) which can have better heat resistance and mechanical properties than polyethylene terephthalate, and which can be used to make films, fibers, and the like.

In refinery streams derived from petroleum or coal, dimethylnaphthalenes are present as isomeric mixtures which are difficult and costly to separate. Hence, techniques for producing specific dimethylnaphthalenes alone or in admixture with one or two other specific isomers are highly desirable. One promising process is to catalytically cyclize one or more alkenylbenzenes into the corresponding dialkyltetralins, i.e., dialkyltetrahydronaphthalenes, which are then dehydrogenated to the corresponding dialkyl-naphthalenes. A mixture of such dialkyl-naphthalenes, such as a mixture or triad of 1,6-, 1,5-, and/or 2,6-dimethylnaphthalenes, can then be isomerized to a single such product, such as 2,6-dimethylnaphthalene. Such a cyclization, dehydrogenation, and isomerization process sequence is described, for example, in EP-A-0 351 074.

The catalyst heretofore employed for the cyclization of the alkenylbenzenes in such process usually is an acidic, ultrastable, Y-type zeolite catalyst in hydrogen form, having a unit cell size of about 24.2 to about 24.7 Angstroms, an SiO_2 to Al_2O_3 molar ratio of about 4:1 to about 10:1, preferably from about 5:1 to about 6:1, and a sodium content of from about 0.05 to about 3.5 weight percent, calculated as elemental sodium and based on the weight of the zeolite. It has now been found, however, that a less acidic catalyst of the same general type, i.e., one having a substantially higher SiO_2 to Al_2O_3 molar ratio and a low Na_2O content provides an unexpectedly improved cyclization of alkenylbenzenes in higher yields and with improved selectivity.

Summary of the Invention

The present invention provides an improved method for catalytically cyclizing alkenylbenzenes to the corresponding methyltetrahydronaphthalenes in relatively higher yields.

This method employs a relatively low acidity, ultrastable, crystalline zeolite Y catalyst that is substantially free of absorbed water, that exhibits Brønsted acidity, but has:

- a unit cell size no greater than about 24.3 Angstroms, and
- a sodium content of no more than about 0.4 weight percent calculated as elemental sodium and based on the weight of the crystalline zeolite, or in terms of the Na_2O to Al_2O_3 bulk molar ratio, in the range of about 0.001:1 to less than about 1:1.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ bulk molar ratio for such a catalyst is at least about 12, and preferably is at least about 30.

The present method is practiced by contacting a liquid alkenylbenzene feed stream containing no more than about 0.1 weight percent water with such a catalyst while maintaining a temperature in the range of about 120°C to about 350°C and a pressure sufficient to maintain the reactants substantially in liquid state during cyclization.

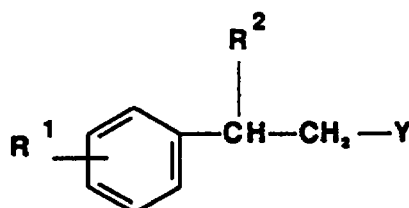
Various other features, advantages, aims, purposes, embodiments, and the like of this invention will be apparent to those skilled in the art from the present specification and appended claims.

Brief Description of the Drawing

In the drawing, FIGURE 1 is a schematic flow diagram illustrating a continuous cyclization process embodying the present invention.

Detailed Description of the Preferred Embodiments

The present invention provides a method for the cyclization of an alkenylbenzene having the formula



wherein R¹ can be a member of the group consisting of hydrogen, methyl, and ethyl, R² can be a member of the group consisting of hydrogen and methyl, and Y is an alkenyl of the group consisting of -CH=CH-CH₃ and -CH₂-CH=CH₂. This method contemplates contacting such an alkenylbenzene, in liquid form and having a water content of no more than 0.1 weight percent, with a solid, particulate cyclization catalyst which is a relatively low acidity, ultrastable hydrogen form of crystalline aluminosilicate zeolite Y, i.e., a molecular sieve of having a cubic, faujasite crystalline structure. The contemplated zeolite Y catalyst has a silica-to-alumina bulk molar ratio of at least 12, a unit cell size no greater than 24.3 Angstroms, a sodium content of no more than about 0.4 weight percent, preferably no more than 0.25 weight percent, calculated as elemental sodium and based on the weight of the zeolite or in terms of the sodium oxide-to-alumina bulk molar ratio in the range of from 0.001:1 to 1:1.

Cyclization of the alkenylbenzene is carried out in the liquid phase, at a temperature in the range of 120°C. to 350°C., and preferably under reflux conditions. Reaction pressure is selected so as to maintain the reactant and the reaction products in the liquid phase while cyclization proceeds. The catalyst contact time with the alkenylbenzene can vary, but is sufficient to produce a liquid product that is enriched in an alkyltetrahydronaphthalene derived from the alkenylbenzene.

The term "relatively low acidity" as used herein in reference to a zeolite useful for the practice of this invention has reference to the relatively few Brønsted acid sites in the crystalline zeolite framework that provide sufficient acidity to catalyze the desired cyclization but without the production of undesirably large amounts of by-products.

Substances that owe their acidity to the presence of protons are termed Brønsted acids. In the case of crystalline aluminosilicates or zeolites, a Brønsted acid site occurs in the crystalline zeolite framework where an aluminum atom surrounded by four oxygen atoms is present. Inasmuch as some of such Brønsted acid sites are neutralized by alkali metal presence in the crystalline framework, the Brønsted acidity of a particular zeolite can be delineated by specifying the bulk molar ratios of SiO₂/Al₂O₃ and Na₂O/Al₂O₃ as set forth hereinabove. In terms of the number of framework Brønsted acid sites per unit cell of the crystalline zeolite catalyst, for the purposes of the present method the catalyst has an average of no more than about 10 framework Brønsted acid sites, preferably no more than about 4 such sites, per unit cell.

The term "ultrastable" as used herein in reference to a zeolite has reference to a zeolite which has been thermally stabilized by dealumination to produce a synthetic zeolite having much improved resistance to degradation under acid and hydrothermal conditions.

The term "zeolite Y" as used herein in reference to the contemplated crystalline aluminosilicate molecular sieve has reference to a zeolite which has the characteristic framework structure of the faujasite mineral class.

The term "bulk molar ratio" as used herein denotes the molar ratio of the designated moieties regardless of whether present in the crystalline framework of the molecular sieve or not.

The ultrastable, zeolite Y employed as a catalyst in the process of the present invention is a low alumina (Al₃O₃)-containing, low sodium (or low sodium oxide)-containing Y- type molecular sieve material that is in hydrogen form and has relatively low acidity. The catalyst pore windows or apertures are defined by twelve tetrahedral atoms. The catalyst framework alumina concentration for such a zeolite is also indicated in part by the unit cell size which, as measured by x-ray diffraction, is no more than 24.3 Angstroms. The SiO₂ to Al₂O₃ bulk molar ratio is above 12, and preferably is at least 30. Expressing the sodium content in terms of sodium oxide, the Na₂O to Al₂O₃ bulk molar ratio is in the range of 0.001 to less than 1, preferably in the range of 0.01 to 0.05.

It is also important for the zeolite catalyst used in the process of this invention to have a relatively low sodium content, as reported in terms of sodium oxide, of less than 0.4 weight percent (on zeolite weight basis), and preferably less than 0.25 weight percent.

A presently preferred ultrastable, zeolite Y having such a combination of low acidity, cell size, Na_2O -to- Al_2O_3 and SiO_2 -to- Al_2O_3 molar ratios, and Na_2O content is available commercially under the trade designation "Conteka CBV 760" from the Conteka Company, Leiden, The Netherlands. This particular catalyst is in powder form and has a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ bulk molar ratio of 0.05, a $\text{SiO}_2/\text{Al}_2\text{O}_3$ bulk molar ratio of 50, and a sodium content of 0.075 weight percent, calculated as elemental sodium and based on the weight of the zeolite. This catalyst has a unit cell size of 24.2 Angstroms and a surface area of 720 m^2/g . Another suitable such zeolite Y catalyst is available commercially from P Q Corporation, Valley Forge, Pa, under the trade designation "Valfor CP 301 - 26". This particular catalyst is in powder form and has a unit cell size of 24.25 Angstroms, an $\text{SiO}_2/\text{Al}_2\text{O}_3$ bulk molar ratio of 80, a sodium content of 0.023 weight percent, calculated as elemental sodium and based on the weight of the zeolite, and a surface area of 775 m^2/g . The $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ bulk molar ratio for this particular catalyst is 0.02.

The present zeolite catalyst, as used in the present cyclization process, can be either in a powdered form or in a granular form. A powdered catalyst is conveniently mechanically dispersed by mixing action in the liquid phase reactant employed. When in a granular form, the granule size can vary widely, such as from 0.079 cm to 2.54 cm (1/32" to 1 inch) in average maximum diameter, the exact size in any given instance being influenced by the choice of particular fixed-bed reactor wherein the granular form is to be employed and through which the liquid phase reactant is circulated. As used herein, the term "granular form" is generic to porous structures having the various possible physical shapes, and made by the various possible preparation methods, including compacting, extruding, and the like, and such term is inclusive of both supported and unsupported zeolite catalyst forms.

When supported, the zeolite Y catalyst can be supported on a porous refractory inorganic oxide that is inert under the cyclization conditions employed. Illustrative such oxides include silica, alumina, silica-alumina, magnesia, bentonite or other such clay, and the like. Presently preferred such oxides are silica, alumina, and silica-alumina. In such a supported catalyst, the zeolite can comprise at least 10 weight percent of the total supported catalyst up to 90 weight percent thereof with a present preference being to employ a quantity of zeolite that is in the range of 20 to 80 weight percent thereof.

Preferred alkenylbenzenes for use in the practice of the method of this invention are 5- (monomethylphenyl)-pent-1-ene, 5-(monomethylphenyl)-pent-2-ene, 5-(phenyl)-hex-1-ene, 5-(phenyl)-hex-2-ene, and mixtures thereof. Examples include 5-(o-, m-, or p- tolyl)-pent-1- or 2-ene, and 5-phenyl-hex-1-or -2-ene.

To minimize production of isomeric product mixtures, it is presently preferred to employ as the reactant feedstock one which is comprised of at least about 90 weight percent on a total feedstock weight basis of a specific alkenylbenzene, exclusive of any solvent that may be present, and more preferably which is comprised of at least about 98 weight percent of such an alkenylbenzene. Most preferably, such a feed comprises a substantially pure alkenylbenzene compound. By the term "substantially pure" as used herein reference is had to a composition which consists of at least 99 weight percent on a 100 weight percent basis of a single compound.

A presently most preferred alkenylbenzene for practicing the method of this invention is 5-(o-tolyl) pent-2-ene (OTP).

The feed used in the practice of this invention should be substantially free of moisture and of other non-hydrocarbon components. The presence of water temporarily deactivates the zeolite catalyst when operating at temperatures of less than 230 °C. Non-hydrocarbon components can be, or can contain or form, agents which poison the catalyst. Examples of such components or agents include amines, metal cations, and the like.

To cyclize an alkenylbenzene in accord with this invention, one contacts such compound with the ultrastable zeolite Y catalyst as herein described while maintaining the resulting admixture at a temperature in the range of 120 °C to 350 °C and at a pressure sufficient to maintain the hydrocarbon reactants substantially in a liquid phase for a time period sufficient to enrich the product with the corresponding alkyltetrahydronaphthalene.

Preferred cyclization temperatures are in the range of 160 to 250 °C. Since the cyclization occurs in the liquid phase, pressure is not critical to the reaction and is dictated primarily by the reaction temperature. During a cyclization reaction, reaction pressure is preferably adjusted to maintain the reactants substantially in a liquid phase. Suitable reaction pressures can be in the range of 17 kPa (2.5 psia) to 3620 kPa (525 psia).

In general, the quantity of the zeolite catalyst employed in a reaction zone for cyclization is that sufficient to be catalytically effective. Catalyst concentration can be varied to optimize the reaction rate.

Concentrations of the zeolite catalyst in the range of 0.1 to 10 weight percent based on total reactor charge are presently preferred, with a catalyst concentration in the range of 0.3 to 2 weight percent (same basis) being more preferred; however, larger and smaller amounts of the catalyst can be employed, if desired.

The cyclization of the alkenylbenzenes to alkyltetrahydronaphthalenes can be carried out batch-wise, continuously, or semicontinuously, as desired. During cyclization, the alkenylbenzene preferably is comingled with the corresponding, preformed alkyltetrahydronaphthalene.

A continuous cyclization process is schematically illustrated in FIGURE 1. Reactor 10 is equipped with agitator 12, reflux column 14 and overhead condenser 16. Alkenylbenzene feedstock from an appropriate source 18 is fed via line 20 to reactor 10 that is maintained at steady state reflux conditions containing a boiling liquid admixture 22 of reactants and reaction products together with the particulate zeolite catalyst suspended therein. The relatively lower boiling feedstock is introduced into the reactor below the liquid level therein while the cyclized product is withdrawn from the reactor 10 via reflux column 14 and is conveyed to overhead condenser 16 via line 24. The withdrawn product is condensed in condenser 16 and a portion thereof is returned to reactor 10 by means of reflux line 26 while the remainder is transported to product storage 30 via product line 28. The relatively high activity of the presently contemplated catalysts permits the illustrated "heavies recycle" without loss of feedstock to the reflux column. That is, the feedstock is converted to a cyclized product before the feedstock can be flashed under the temperature and pressure conditions prevailing in the reactor. Analyses of cyclized product obtained utilizing the aforesaid "heavies recycle" technique have indicated less than about 1 weight percent of feedstock material in the cyclized product.

Batch cyclization is preferably carried out until substantially all of the alkenylbenzene present is converted. Thereafter, the product dimethyltetrahydronaphthalene can be readily separated from the reaction mass by flash distillation.

To carry out a batch type process, a stirred tank reactor where the zeolite catalyst is present in powdered form can be utilized. At startup, an initiator batch is preferably produced in such a reactor. Such a batch comprises the zeolite catalyst and a non-reactive hydrocarbon which is substantially in a liquid phase under the contacting conditions. While the choice of such a non-reactive hydrocarbon can vary widely and is not critical, it is presently preferred to employ as such hydrocarbon a dimethyltetrahydronaphthalene, particularly the specific dimethyltetrahydronaphthalene sought to be produced in the batch process.

The reactant feed, which is substantially free of moisture and other non-hydrocarbon components as above indicated, is added to a batch reactor that preferably already contains such an initiator batch therein. The presently most preferred feed is substantially pure OTP.

Feed addition is carried out at a rate which allows heat removal and control of temperature in the reactor so that the reactant and reaction product temperature in the liquid phase is maintained at a level which is within the above indicated temperature range.

After a chosen quantity of the feed has been so added and has been converted to the corresponding dialkyltetrahydronaphthalene, the latter is removed from the reactor by flash distillation. Left behind in the tank is a "heel" composition that includes the zeolite catalyst, optionally some residual dimethyltetrahydronaphthalene product, and hydrocarbon by-products having molecular weights higher than 160, i.e., above the molecular weight of a dialkyltetrahydronaphthalene. Such hydrocarbon by-products typically comprise dimers of the alkenylbenzene and the produced dialkyltetrahydronaphthalene.

During the post-reaction flash distillation, at least about 60 weight percent of the dimethyltetrahydronaphthalene, based on the total product dimethyltetrahydronaphthalene estimated to be present in the reactor at the termination of the batch reaction, is removed.

Thereafter, an additional chosen quantity of the feed is added to the heel composition present in the tank. As before, the feed addition rate is preferably such as to allow heat removal during cyclization and temperature control. After the desired conversion of the feed is achieved, the flash distillation step is repeated to remove additional product from the reactor.

Such a batch step sequence can be repeated for a number of cycles as long as catalyst activity can be maintained. With repeated cycles, however, a build-up of the above indicated hydrocarbon by-products to an equilibrium level may occur in reactor.

When the level or quantity of such by-products has reached some chosen point, a cracking procedure can be carried out concurrently or sequentially to decompose relatively larger molecules into smaller, lower boiling molecules, some of which are alkenylbenzenes. At the same time, such alkenylbenzenes present react and cyclize to dialkyltetrahydronaphthalenes. In such a procedure, if performed sequentially, the heel composition that is produced as a result of a preceding batch cycle or cycles as above characterized is heated to a temperature in the range of 180°C to 350°C and at a pressure sufficient to maintain such heel composition substantially in a liquid phase, so as to convert the indicated dimers in such heel composition

into additional dialkyltetrahydronaphthalene which is then removed by flash distillation from the reactor. Thus the same zeolite Y catalyst serves two functions. Yields of dimethyltetrahydronaphthalene are thereby maximized.

In one presently particularly preferred mode of practicing the process of this invention, 1,5-dimethyltetrahydronaphthalene is made by cyclizing 5-(o-tolyl)-pent-2-ene (OTP). To that end, an initiator batch comprised of the powdered catalyst and 1,5-dimethyltetrahydronaphthalene is first formed in a stirred tank reactor by 100% conversion of an OTP charge using temperature and pressure conditions as above described. The amount of catalyst used is such that, after the addition of the OTP in the next step (described below), the concentration of the zeolite catalyst is in the aforesaid preferred range.

Next, the substantially pure OTP that is substantially free of moisture and also of non-hydrocarbon components is added to the reactor maintained at a temperature in the range of 160°C to 250°C, and at a pressure sufficient to maintain the reactants in a liquid phase. The OTP addition is carried out at a rate which allows heat removal and control of temperature in the reactor at a chosen reflux level which is within the above indicated temperature range.

The reactor is maintained at such a chosen reflux level while the pressure is gradually reduced to a level which is sufficient to maintain a chosen reflux level until substantially all of the OTP has been converted.

Finally, 75 to 80 weight percent of the thus formed 1,5-dimethyltetrahydronaphthalene is flash distilled from the reactor.

The foregoing conversion steps are then sequentially repeated at least once. As the Examples hereinbelow indicate, this sequence can be repeated at least seven times without noticeable catalyst deactivation; thus, no increase in reaction temperature or in reaction time is needed to complete the OTP conversion in subsequent batches. The amount of useful products produced for seven such batches was 4.1% higher than the amount of useful product produced in a comparable procedure carried out using a more acidic zeolite Y catalyst. Such increase also represents a 49% by weight reduction in final product impurities. In addition, for such seven batches, the cumulative yield of useful components was increased from 85% in such comparable procedure to 90% when using the presently contemplated catalyst. The amount of undesired dimethyltetrahydronaphthalene isomers concurrently decreased from 1.2 percent by weight to an average of about 0.9 percent by weight.

The catalyst employed in the present invention is more active and more stable, and gives higher product purity with higher yield, than is possible with the more acidic catalysts heretofore employed for the cyclization of alkenylbenzenes.

Moreover, the thermal stability of the present catalyst permits multiple successive batch runs to be carried out, each batch using similar conditions without adding additional catalyst. In addition, when the heavy by-products accumulate, they can be selectively converted to useful products by a cracking procedure using the same catalyst and the same reactor. The use of this catalyst in a fixed-bed reactor provides equally positive results.

In this manner the alkenylbenzene feed is rapidly converted to a useful product, thereby avoiding a dangerously high concentration of feed, such as, for example, OTP, in the reactor. The capacity to flash distill and separate desired product from catalyst and heavy by-products, thereby leaving the reactor ready for use in a next batch provides a safe, cost effective, and advantageous process that is efficient to operate.

The zeolite catalyst employed herein exhibits an unusually low isomerization activity. Thus, a reaction product can be maintained for extended periods of time in the presence of the catalyst with substantially no product degradation into isomers. This feature is illustrated in Example 18, below.

A presently preferred class of cyclized products includes dimethyltetrahydronaphthalene isomers which can be readily dehydrogenated. Suitable conversion procedures are known to the prior art.

The present invention is illustrated by the following examples.

In these Examples, the term "useful product" refers to all useful components in a cyclized product, including all dimethyltetrahydronaphthalene (termed DMT) isomers and all dimethylnaphthalene (termed DMN) isomers which can be converted by dehydrogenation and isomerization into the desired 2,6-dimethylnaphthalene. In these examples, such "DMT isomers" are the 1,5-, 1,6-, 2,5- and 2,6-DMT isomers.

Examples 1-16: Comparison of High Alumina Content with Low Alumina Content Acidic, Ultrastable Y-type Zeolite Catalysts

To compare a relatively high alumina content, acidic, ultrastable, Y-type zeolite catalyst ("Catalyst A") with a relatively low alumina content ultrastable, Y-type zeolite catalyst ("Catalyst B"), the following zeolite catalyst materials were used:

TABLE 1

CATALYST CHARACTERISTICS				
Catalyst	Cell Size (Angstroms)	SiO ₂ /Al ₂ O ₃ Bulk Molar Ratio	Na ₂ O Content (Wt.%)	Na ₂ O/Al ₂ O ₃ Bulk Molar Ratio
Catalyst A	24.51	5.1	2.5	0.17
Catalyst B	24.20	42	0.05	0.05

Catalyst A was a catalyst commercially available from the Union Carbide Company, Danbury, CT., under the trade designation "LZ-Y72". Catalyst B was a catalyst commercially available from the Conteka Company under the trade designation "Conteka CBV 760". For each catalyst, the following procedure was used:

A 1000 ml flask fitted with a magnetic stirrer, reflux condenser, and distillation/collection head was charged with 1.8g of powdered catalyst and 150g of 98% by weight (based on total hydrocarbon feedstock) of 5-(o-tolyl) pent-2-ene (OTP). The flask was brought to a pressure of 40.8 kPa (6 psia) and 180-190 °C. at which point the reactor contents were at reflux. Thereafter, the pressure was gradually decreased as the OTP was converted while the temperature and reflux were maintained. This conversion took about 2-4 hours and the product comprised about 88 weight percent (100 weight percent product basis) dimethyl-tetrahydronaphthalene, the remainder being constituted by heavy and light byproducts. The converted OTP in the first 150g batch served as a "heel" composition for the second and subsequent successive batches. The results are compiled in Tables 2 and 3, below.

In Table 2 results with Catalyst A are reported, while in Table 3 results with Catalyst B are reported. The amount of OTP fed and the amount of product produced is shown in each Table along with batch operating conditions.

For the first full batch (#1 in each of Tables 2 and 3), 5.4 g of additional catalyst was introduced into the flask. After reflux was established in the reactor at 180-190 °C, for each batch an additional 440 g of OTP was added over a time period of 2 hours. This procedure is preferred in a larger scale commercial operation because heat generation can be controlled by the rate of OTP addition in this manner. Following the OTP addition, the reaction admixture was maintained at reflux at the above-stated temperature until all of the added OTP was converted as determined by gas chromatography. Typically, about 2-5 hours was required after OTP addition to achieve complete conversion. About 75% of the product produced in each batch was then flash distilled from the reactor, leaving about 25% of the product as the heel for the next batch. The heavy by-products and all the catalyst remained in the heel. For each of Batches 2-7, no additional catalyst was added. The amount of OTP added for each batch was about the same as the amount of cyclized product removed from the previous batch.

TABLE 2
CYCLIZATION OF OTP USING CATALYST A

Example	Batch	Temp, C	Reaction Time(Hr)	Amt.Feed Grams	Amt.Prod Grams	Wt.-% Useful In Product	Wt.-% DMT Isom	Cumulative G Useful/G OTP
1	HEEL	190	4.5	150.0	2.8	88.3	1.03	0.00
2	1	190	4.0	440.0	437.7	92.3	1.12	0.69
3	2	200	7.0	440.0	454.2	92.8	1.07	0.80
4	3	216	8.0	440.0	387.9	92.4	1.17	0.81
5	4	237	2.8	403.0	415.6	90.6	1.34	0.83
6	5	238	2.8	417.0	411.4	90.9	1.27	0.84
7	6	238	2.8	420.6	405.9	91.2	1.22	0.85
8	7	238	2.8	406.6	391.4	91.2	1.22	0.85
TOTALS				3117.2	2906.9			
Average		222	4.3			91.6	1.2	
Batches 1-7								

TABLE 3
CYCLIZATION OF OTP USING CATALYST B

<u>Example</u>	<u>Batch</u>	<u>Temp, C</u>	<u>Reaction Time(Hr)</u>	<u>Amt.Feed Grams</u>	<u>Amt.Prod Grams</u>	<u>Wt.-% Useful In Product</u>	<u>Wt.-% DMT Isom</u>	<u>Cumulative G Useful/G OTP</u>
9	HEEL	180	3	150	1.8	88.8	0.89	0.01
10	1	180	<2.0	448	431.8	94.8	0.91	0.69
11	2	180	<2.0	450	442.5	96.2	0.86	0.80
12	3	180	<2.0	439	412.1	96.0	0.88	0.83
13	4	180	<2.0	420	421.2	95.8	0.90	0.86
14	5	180	<2.0	450	455.2	96.1	0.89	0.88
15	6	180	<2.0	441	443.0	95.6	0.95	0.89
16	7	180	<2.0	451	444.7	95.6	0.89	0.90
TOTALS				3249	052.3			
Average		180	<2.0			95.7	0.90	

In the case of Catalyst A (see Table 2), the catalyst gradually deactivated with successive batch runs, requiring batch temperature increases or reaction time increases to compensate for such catalyst deactivation. The weight percent of useful product in each batch was in the range of 90.6 to 92.8 weight percent, based on total batch product. The average weight percent of useful product produced was 91.6% Batches 1 through 7. The amount of undesired DMT isomers was in the range of about 1.07% to about 1.34%, and averaged 1.2%. The cumulative amount of useful product removed from the system is listed in the far right column of the Table 2. The yield in early runs was low since a heel of the product remains in the system. After 7 full batches, the cumulative amount of useful product obtained was 0.85 grams/gram of OTP (85%).

In the case of Catalyst B (see Table 3), the relatively higher activity thereof allowed operation at 180 °C with shorter reaction times than was possible with Catalyst A. In the 7 batches, no catalyst deactivation was observed, so no increase in temperature or reaction time was necessary to complete the OTP conversion. The weight percent of useful products for the 7 batches was in the range of 94.8% to 96.2%, and averaged 95.7%. This is an average increase of 4.1% over the yield obtained with Catalyst A in Examples 1-8. This represents a 49% reduction in impurities for the final useful product. In addition, the cumulative yield of components in the useful product increased from 85% for such comparison Catalyst A to 90% for the present improved Catalyst B. The amount of undesired DMT isomers decreased from 1.2% using the comparison Catalyst A to an average of 0.9% for Catalyst B. Thus, Catalyst B was more active under the present process conditions, more stable, and gave higher product purity as well as higher yield than Catalyst A.

Example 17: Cracking of Heavy By-Products with Low Aluminum Ultrastable Y-Catalyst

Following the seven batch runs described in Examples 9-16, a residue remained in the reactor vessel. This residue consisted mainly of high molecular weight dimers formed by the reaction of OTP with DMT. These dimers were cracked back to DMT by extended heating solely in the presence of the catalyst at relatively low pressure. The DMT, once thus formed, was flash distilled out of the reactor.

The residue contained 7.2 g of the Catalyst B which had previously been used for the seven cycles of DMT production from OTP. The conversion was carried out at 220 °C and 17 KPa (127 Torr, 2.5 psia) for 2 hours. The heavy by-product dimers comprised 71% (138.6 g) of the heel composition. The balance of the heel composition was DMT and DMN isomers.

A distilled product (128 g) containing 92.1% (117.9 g) useful components was obtained. The residue in the reactor contained 26.7 wt% useful components and 66.5% heavy dimers. Thus, 67.8 wt% of the heavies in the residue were converted to useful product with a selectivity of 88 wt%. This additional amount of useful product represents a 4 wt.-% increase in yield to 0.94 lbs of useful product/lb of 98 wt.-% pure OTP.

This procedure is, in practice, an extension of the normal flash distillation procedure and only requires additional reaction time.

The results of this cracking procedure are shown in Table 4, below.

TABLE 4

CONVERSION OF HEAVY BY-PRODUCTS USING CATALYST B					
Feedstock	Total	Useful Product	Undesired DMT Isomers	Heavies	Other
-Grams	195	53.2	0.5	138.6	2.7
-Wt%	100	27.3	0.3	71.1	1.4
Product-Distilled					
-Grams	128	117.9	2.2	0.2	7.8
-Wt%	65.6	92.1	1.7	0.1	6.1
Product-Residue					
-Grams	67	17.9	0.4	44.6	4.2
-Wt%	34.4	26.7	0.5	66.5	6.3
Total-Product Wt	195	135.8	2.5	44.7	12.0

Example 18: Low Isomerization Activity of Presently Contemplated Low Alumina, Ultrastable Y-Type Catalyst

A batch conversion of OTP was conducted with a fresh sample of the Catalyst B and using a catalyst loading as employed in the procedure of Examples 9-16. Specifically, the present process procedure employed 10.2 g of previously prepared dimethyltetrahydronaphthalene, 94.4 g of OTP, and 0.32 g of Catalyst B. The temperature was 190 °C, and the pressure was 17 KPa (203 Torr, 3.9 psia). A complete conversion of OTP was observed after 2 hours with 94.9% selectivity to useful product. After 18 hours, the conversion of OTP was still 100% with selectivity to useful product being 94.1%.

Following complete conversion of the OTP in two hours, the reactor was allowed to reflux at 190 °C for an additional 16 hours to simulate a very slow flashing step. The results are shown in Table 5 below. These results indicate that over a period of 16 hours the loss of useful products was only 0.6%. No increase in the amount of undesired DMT isomers was observed.

TABLE 5

RESISTANCE TO ISOMERIZATION AFTER CYCLIZATION OF 5-(o-TOLYL)PENTENE-2 USING LOW ALUMINA ULTRASTABLE Y-TYPE CATALYST					
Batch	Temp, °C	Reaction Time(Hr)	Wt.-% OTP	Wt.-% Useful In Product	Wt.-% DMT Isom
1	Feed	0	74	24.6	0.2
	190	2	0	94.8	0.8
	190	18	0	94.2	0.7

Examples 19-24: Additional Batch Runs Made With Used Low Alumina Ultrastable Y-Type Catalyst

Batch runs were made in a manner similar to that employed in Examples 9-16 employing a previously used Catalyst B from such Examples. Results are shown in Table 6, below. Temperature variations were made to observe the range of operability of the catalyst.

Batch run No. 8 was made under the same conditions as Batches Nos. 1 through 7 and demonstrates that the cracking of heavy by-products (Example 17, Table 4) was not detrimental to catalyst activity. Batch 9 indicates that an increase in temperature to 190 °C is not detrimental to catalyst performance. In Batch 10, the operation at 160 °C resulted in significantly lower reaction rates yielding incomplete conversion. The presence of a small amount of water in the distillate of Batch 10 indicated some catalyst poisoning. In Batch 11, the temperature of the catalyst was increased to accelerate the reaction and to drive off water from the previous batch. In Batch 12, the catalyst activity was noted to be lower than fresh catalyst, but still relatively high, yielding high conversion in 5.5 hours at 180 °C. Finally, Batch 13 was conducted at a high temperature and demonstrates that even at such conditions selectivity and high yields could be obtained. For the entire series of 13 batch runs, the total OTP converted by the catalyst was 812 grams per gram of catalyst.

In all of these batch runs, the catalyst was Catalyst B from the first batch. The amount of catalyst was 7.2 grams. At the end of each batch run, the liquid in the reactor was subjected to flash distillation to leave a residue that was employed as the heel for the next succeeding batch. The residue remaining in the reactor at the end of 13 batch runs was 70.6 g. For all 13 batches, 5928 g of feedstock OTP were used and 5848 g of useful product was recovered by flash distillation. Total catalyst productivity was determined by the fact that 5848 g of OTP were converted with 7.2 g of Catalyst B so that 812 g of useful product per gram of catalyst was obtained.

TABLE 6
BATCH CYCLIZATION OF 5-(o-TOLYL)PENTENE-2 USING A
USED LOW ALUMINA ULTRASTABLE Y-TYPE CATALYST TO
DEMONSTRATE CATALYST STABILITY

<u>Example</u>	<u>Batch</u>	<u>Temp,</u> <u>C</u>	<u>Reaction</u> <u>Time(Hr)</u>	<u>Feedstock</u> <u>G Residue</u>	<u>G OTP</u>	<u>Dist.Prod</u> <u>Grams</u>	<u>Wt.-% OTP</u> <u>In Prod.</u>	<u>Wt.-% Useful</u> <u>In Prod.</u>	<u>Wt.-%</u> <u>DMT Isom</u>
19	8	180	2.5	71.6	450.0	445.0	0.0	95.3	1.0
20	9	190	2.5	82.5	449.9	439.0	0.0	95.2	1.0
21	10	160	12.3	84.3	433.7	431.9	18.5	71.7	0.7
22	11	170-246	9.0	83.4	449.9	450.2	0.1	92.3	1.1
23	12	180	5.5	83.2	446.3	446.4	0.5	92.0	1.1
24	13	246	2.5	70.6	449.9	462.5	0.0	92.1	1.2

Example 25: Continuous Cyclization of 5-(o-Tolyl)Pentene (OTP)

OTP was continuously fed to a stirred tank reactor equipped with an overhead condenser and maintained at reflux temperature for the reactor contents. The reflux temperature was modulated by adjusting the system pressure.

The product (DMT) was constantly removed from the overhead as a distillate. The heavy byproducts were retained in the reactor where they ultimately reached an equilibrium concentration, preventing further heavy formation.

The data presented in Table 7, below, illustrate 6 days of operation. The initial catalyst charge was a "low activity" sample of the Conteka 760 catalyst which required a reaction temperature of 210°C in the batch mode. After making 5 batch runs with this low activity catalyst, the hydrocarbon product from the 5th batch run was used as the reaction medium for the continuous cyclization. On the first day of operation (first column), the distillate contained 94% useful components (2,6-Triad DMT + DMN, without the xylene impurity present in the feed) and only 1% of the sum of OTP and an intermediate convertible to product. During the first day of operation, the heavies in the reactor increased such that the overall yield for the first day (noted at the bottom of the table) was only 81.5% of the 2,6-triad. On Days 2-6 the distillate quality was similar to the first day. However, the heavy formation in the reactor decreased, and on Day 3, addition of fresh catalyst actually yielded a net loss of heavies in the system (negative yield).

The overall results for the continuous run after 6 days (55 hours) are presented in the far right column of Table 7. The average distillate contained 93.3% useful components (xylene-free basis) and the overall yield of the 2,6-triad DMT + DMNs was 92.5%.

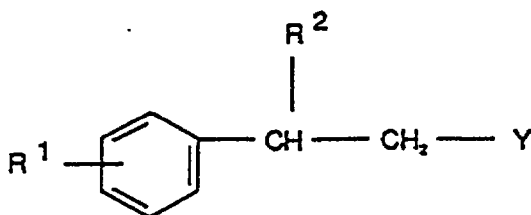
TABLE 7
CONTINUOUS CYCLIZATION IN A STIRRED TANK REACTOR

	Day						For Overall Run
	1	2	3	4	5	6	
Feed G/Hr (Approx.)	4	4	4	4	4	4	
Type Catalyst (Conteka CBV 760)	Used for 5 Batches Low Activity		Add 3.5 G Fresh High Activity				
G Low Activity Cat.	7.1	7.1	7.1	7.1	7.1	7.1	7.1
G High Activity Cat.	0	0	3.5	3.5	3.5	3.5	3.5
wt.-% Cat. in Reactor (Total)	1.2	1.2	2	2	2	2	2
Ave. Temp., °C	218	238	225	225	240**	230-240	218-240
Ave. Press, psia	6.4	6.2	6.4	6.4	9-12	7-11	6-12
Hrs. on Feed for Day	6.7	13	10.1	8.1	10	7.1	55
G of Feed into Reactor	1259	2902	2235	1981	1670	1861	11916
Cumulative-End of Day							
Hrs. on Low Act. Cat.	37	50	60	68	78	85	85
Hrs. On Hi Act. Cat.	-	-	10	18	28	35	35
G Feed into Reactor	3644	6546	8781	10762	12432	14301	14301
G Feed/G Cat.	513	922	828	1015	1173	1349	1349
Average Product (Distillate) Composition for Each Day -- Weight Percent							
o-Xylene	1.5	1.1	1.1	1.1	0.8	0.9	1.1
SAT OTP	1.7	1.5	2.4	2.2	2.9	2.1	2.1
OTP + Intermed.	1.0	3.2	0.9	1.1	0.5	0.8	1.4
2,6-Triad DMT + DMN*	92.6	90.7	92.9	93.0	91.7	93.4	92.3
2,7-Triad DMT	0.9	0.9	0.8	0.8	0.9	0.9	0.9
Heavy	0.0	0.0	0.1	0.2	0.6	0.0	0.1
Other	2.3	2.5	1.8	1.5	2.6	1.8	2.1
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0
*2,6-Triad w/o Xylene	94.0	91.7	93.9	94.0	92.5	94.3	93.3
Average Daily Yields -- Including Change in Reactor Composition and Quantity G Component/100 G Tolympentenes							
Sat. OTP	1.5	1.5	2.7	2.2	3.0	2.0	2.1
OTP	0.9	3.2	1.0	1.1	0.5	0.8	1.4
2,6-Triad DMT + DMN	81.5	89.1	92.7	93.2	96.0	88.5	92.5
2,7-Triad DMT	0.8	0.9	0.9	0.8	0.9	0.9	0.9
Heavy	13.3	2.8	-9.3	1.1	-3.2	6.2	1.0
Other	2.0	2.5	1.9	1.5	2.7	1.7	2.1
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0



Claims

1. A method for cyclizing an alkenylbenzene having the formula



(I)

wherein

R¹ is hydrogen, methyl or ethyl,

R² is hydrogen or methyl, and

Y is -CH=CH-CH₃ or -CH₂-CH=CH₂

which comprises contacting said alkenylbenzene in liquid form with a solid cyclization catalyst constituted by a relatively low acidity, ultrastable, hydrogen form of crystalline aluminosilicate zeolite Y having a silica-to-alumina bulk molar ratio of at least 12:1, an average of no more than 10 framework Brønsted acid sites per unit cell, a unit cell size no greater than 24.3 Angstroms, and a sodium content of no more than 0.4 percent by weight, calculated as elemental sodium and based on the weight of the zeolite; or in terms of the sodium oxide-to-alumina bulk molar ratio in the range of 0.001:1 to less than 1:1, at a temperature in the range of 120°C to 350°C; and at a pressure sufficient to maintain the reactants substantially in liquid state during cyclization.

2. The method of claim wherein said temperature is in the range of 160°C to 250°C.

3. The method of claim 1 or claim 2 wherein said alkenylbenzene is cyclized in the presence of preformed dialkyltetrahydronaphthalene.

4. The method of any preceding claim wherein said zeolite catalyst is a powder, and said contacting occurs in a stirred tank reactor.

5. The method of any preceding claim wherein said zeolite catalyst is supported on a porous refractory inorganic oxide.

6. The method of claim 5 wherein the zeolite catalyst constitutes 10 to 90 percent by weight of the total weight of supported catalyst.

7. The method of any preceding claim practiced continuously.

8. The method of any of claims 1 to 6 practiced batchwise.

9. A method according to any preceding claim which comprises the steps of:

(A) initially forming in a stirred tank reactor an initiator batch comprising a non-reactive hydrocarbon which is in a liquid phase at a temperature in the range of 160°C to 250°C and at a pressure in the range of 17 kPa to 3620 kPa (2.5 to 525 pounds per square inch absolute), and a powdered cyclization catalyst constituted by a relatively low acidity, ultrastable hydrogen form of crystalline aluminosilicate zeolite Y having a silica-to-alumina bulk molar ratio of at least 12:1, an average of no more than 10 framework Brønsted acid sites per unit cell, a unit cell size no greater than 24.3 Angstroms, and a sodium content of no more than 0.4 percent by weight, calculated as elemental sodium and based on the weight of said zeolite, or in terms of the sodium oxide-to-alumina bulk molar ratio in the range of 0.001:1 to less than 1 and

(B) adding to said initiator batch in said stirred tank reactor under liquid phase conditions an alkenylbenzene of formula (I) as defined in claim 1, said alkenylbenzene being substantially free of non-hydrocarbon components, and contacting said alkenylbenzene with said zeolite catalyst at a



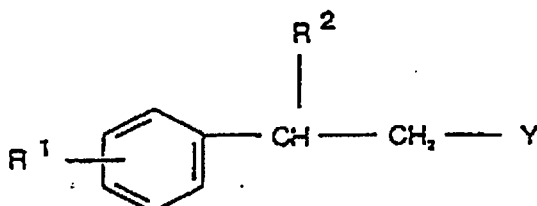
temperature in the range of 120°C to 350°C at a pressure sufficient to maintain the reactants substantially in liquid state during cyclization.

- 5 10. The method of claim 9 wherein said non-reactive hydrocarbon comprises an alkyltetrahydronaphthalene.
11. The method of claim 9 or claim 10 wherein said catalyst concentration is in the range of 0.3 to 2 weight percent.
- 10 12. The method of any of claims 9 to 11 wherein produced alkyltetrahydronaphthalene is removed from said tank reactor by flash distillation while leaving in said tank reactor a heel composition comprising said zeolite catalyst, residual dialkyltetrahydronaphthalenes, and hydrocarbon by-products having molecular weights higher than that of said residual dialkyltetrahydronaphthalenes.
- 15 13. The method of claim 12 wherein thereafter additional alkenylbenzene is added to said heel composition, said alkenylbenzene in liquid form is contacted at a temperature in the range of 120°C to 350°C with said zeolite catalyst for a time period sufficient to produce a liquid product enriched in said alkyltetrahydronaphthalene, after which said flash distillation is repeated.
- 20 14. The method of claim 12 wherein said heel composition in said tank reactor is heated to a temperature in the range of 180°C to 350°C at a pressure sufficient to maintain said heel composition substantially in a liquid phase, thereby cracking said composition and forming dimethyltetrahydronaphthalene which is concurrently removed by flash distillation from said tank reaction zone.
- 25 15. The method of any of claims 9 to 14 practiced continuously.
16. The method of any preceding claim wherein said alkenylbenzene is a 5-(0-tolyl)-pent-2-ene, or a 5-(0-tolyl)-pent-1-ene.
- 30 17. A batch method according to claim 1 for making 1,5-dimethyltetrahydronaphthalene by cyclizing 5-(0-tolyl)-pent-2-ene comprising the steps of
- (a) contacting an aliquot of substantially pure 5-(0-tolyl)-pent-2-ene with a catalytically effective amount of a solid cyclization catalyst constituted by a substantially neutral, ultrastable, hydrogen form of crystalline aluminosilicate zeolite Y having a silica-to-alumina bulk molar ratio of at least 12:1, an average of no more than 10 framework Brønsted acid sites per unit cell, a unit cell size no greater than 24.3 Angstroms, and a sodium content of no more than 0.4 percent by weight calculated as elemental sodium and based on the weight of said zeolite Y or in terms of the sodium oxide-to-alumina bulk molar ratio in the range of 0.001:1 to less than 1:1, at a temperature in the range of 120°C to 350°C at a pressure sufficient to maintain the reactants substantially in liquid state during cyclization for a time period sufficient to substantially convert said 5-(0-tolyl)-pent-2-ene into a liquid composition enriched in 1,5-dimethyltetrahydronaphthalene;
- 35 (b) adding to said liquid product another aliquot of substantially pure 5-(0-tolyl)-pent-2-ene while maintaining said temperature and said liquid phase conditions, said adding being carried out at a rate which allows heat removal and control of said temperature range;
- 40 (c) maintaining said reflux temperature levels while reducing said pressure at a rate sufficient to maintain said reflux level until said 5-(0-tolyl)-pent-2-ene is substantially converted into a liquid product enriched in 1,5-dimethyltetrahydronaphthalene; and
- 45 (d) flash distilling from said liquid product at least about 70 weight percent of said 1,5-dimethyltetrahydronaphthalene therein and leaving a residual liquid composition.
- 50 18. The method of claim 17 wherein the step sequence of said steps (b), (c) and (d) is repeated at least once.
- 55 19. The method of claim 17 or claim 18 wherein, after step (d), said residual composition in said reaction zone is further processed by heating said composition to a temperature in the range of 180°C to 350°C while maintaining a pressure sufficient to maintain said composition substantially in a liquid phase and concurrently removing by flash distillation from said reaction zone 1,5-dimethyltetrahydronaphthalene.



Patentansprüche

1. Verfahren zur Cyclisierung eines Alkenylbenzols der Formel



(I)

worin

R¹ Wasserstoff, Methyl oder Ethyl ist,

R² Wasserstoff oder Methyl ist, und

Y -CH=CH-CH₃ oder -CH₂-CH=CH₂ ist,

welches umfaßt, daß das Alkenylbenzol in flüssiger Form mit einem festen Cyclisierungskatalysator, der eine relativ schwach acide, ultrastabile Wasserstoff-Form eines kristallin Alumosilikat-Y-Zeoliths beinhaltet, welcher ein massenbezogenes Siliciumdioxid:Aluminiumoxid-Molverhältnis von mindestens 12:1 aufweist, im Gitter im Durchschnitt nicht mehr als 10 Brönsted-Säure-Zentren pro Elementarzelle aufweist, eine Elementarzellengröße von nicht mehr als 24.3 Angström aufweist und einen als elementares Natrium berechneten und auf das Gewicht des Zeoliths bezogenen Natrium-Gehalt von nicht mehr als 0,4 Gew.-% aufweist, oder welcher ausgedrückt als massenbezogenes Natrium-oxid:Aluminiumoxid-Molverhältnis im Bereich von 0,001:1 bis kleiner als 1:1 liegt, bei einer Temperatur im Bereich von 120 °C bis 350 °C und einem Druck, welcher ausreicht, und die Reaktanten während der Cyclisierung im wesentlichen im flüssigen Zustand zu halten, in Berührung gebracht wird.

2. Verfahren gemäß Anspruch, worin die Temperatur im Bereich von 160 °C bis 250 °C liegt.

3. Verfahren gemäß Anspruch 1 oder 2, worin das Alkenylbenzol in Gegenwart von bereits gebildetem Dialkyltetrahydronaphthalin cyclisiert wird.

4. Verfahren gemäß irgendeinem der vorangehenden Ansprüche, worin der Zeolith-Katalysator als Pulver vorliegt und das In-Berührung-Bringen in einem Tank-Reaktor unter Rühren stattfindet.

5. Verfahren gemäß irgendeinem der vorangehenden Ansprüche, worin der Zeolith-Katalysator auf einem porösen, feuerfesten, anorganischen Oxid-Träger vorliegt.

6. Verfahren gemäß Anspruch 5, worin der Zeolith-Katalysator 10 bis 90 Gew.-% des Gesamtgewichts des Träger-Katalysators ausmacht.

7. Verfahren gemäß irgendeinem der vorangehenden Ansprüche, welches kontinuierlich durchgeführt wird.

8. Verfahren gemäß irgendeinem der Ansprüche 1 bis 6, welches diskontinuierlich durchgeführt wird.

9. Verfahren gemäß irgendeinem der vorangehenden Ansprüche, welches die Schritte umfaßt, daß:

(A) in einem Tank-Reaktor unter Rühren zuerst eine Initiator-Charge bereitet wird, die einen nicht-reaktiven Kohlenwasserstoff, der bei einer Temperatur im Bereich von 160 °C bis 250 °C und einem Druck im Bereich von 17 kPa bis 3620 kPa (2,5 bis 525 Pfund pro Quadratzoll absolut) in flüssiger Phase vorliegt, sowie einen pulverisierten Cyclisierungskatalysator umfaßt, der eine relativ schwach acide, ultrastabile Wasserstoff-Form eines kristallin Alumosilikat-Y-Zeoliths beinhaltet, welcher ein massenbezogenes Siliciumdioxid:Aluminiumoxid-Molverhältnis von mindestens 12:1 aufweist, im Gitter im Durchschnitt nicht mehr als 10 Brönsted-Säure-Zentren pro Elementarzelle aufweist, eine Elementarzellengröße von nicht mehr als 24.3 Angström aufweist und einen als elementares Natrium berechneten und auf das Gewicht des Zeoliths bezogenen Natrium-Gehalt von nicht mehr als 0,4 Gew.-% aufweist, oder welcher ausgedrückt als massenbezogenes Natrium-oxid:Aluminiumoxid-Molverhältnis im Bereich von 0,001:1 bis kleiner als 1 liegt, und



(B) zu dieser Initiator-Charge in dem Tank-Reaktor unter Rühren sowie unter Bedingungen, unter denen eine flüssige Phase vorliegt, ein Alkenylbenzol der Formel (I) gemäß der Definition in Anspruch 1 zugegeben wird, wobei dieses Alkenylbenzol im wesentlichen frei von Nicht-Kohlenwasserstoff-Komponenten ist, und dieses Alkenylbenzol mit dem Zeolith-Katalysator bei einer Temperatur im Bereich von 120 °C bis 350 °C und einem Druck, der ausreicht, um die Reaktanten während der Cyclisierung im wesentlichen in flüssiger Phase zu halten, in Berührung gebracht wird.

10. Verfahren gemäß Anspruch 9, worin dieser nicht-reaktive Kohlenwasserstoff ein Alkyltetrahydronaphthalin umfaßt.

11. Verfahren gemäß Anspruch 9 oder 10, worin die Katalysator-Konzentration im Bereich von 0,3 bis 2 Gew.-% liegt.

12. Verfahren gemäß irgendeinem der Ansprüche 9 bis 11, worin das erzeugte Alkyltetrahydronaphthalin aus dem Tank-Reaktor mittels Flash-Destillation entfernt wird, wobei in diesem Tank-Reaktor eine Rückstands-Zusammensetzung verbleibt, die den Zeolith-Katalysator, zurückgebliebene Dialkyltetrahydronaphthaline und Kohlenwasserstoff-Nebenprodukte mit Molekulargewichten, die über den Molekulargewichten der zurückgebliebenen Dialkyltetrahydronaphthaline liegen, umfaßt.

13. Verfahren gemäß Anspruch 12, worin anschließend zusätzliches Alkenylbenzol zu dieser Rückstands-Zusammensetzung gegeben wird, wobei das Alkenylbenzol in flüssiger Form bei einer Temperatur im Bereich von 120 °C bis 350 °C mit dem Zeolith-Katalysator innerhalb eines Zeitraums, der zur Erzeugung eines flüssigen, an besagtem Alkyltetrahydronaphthalin angereicherten Produktes ausreicht, mit dem Zeolith-Katalysator in Berührung gebracht wird, worauf die Flash-Destillation wiederholt wird.

14. Verfahren gemäß Anspruch 12, worin die Rückstands-Zusammensetzung im Tank-Reaktor auf eine Temperatur im Bereich von 180 °C bis 350 °C bei einem Druck erhitzt wird, welcher ausreicht, um diese Rückstands-Zusammensetzung im wesentlichen in flüssiger Phase zu halten, wobei diese Zusammensetzung gekrackt wird und Dimethyltetrahydronaphthalin gebildet wird, welches gleichzeitig mittels Flash-Destillation aus der Reaktionszone dieses Tanks entfernt wird.

15. Verfahren gemäß irgendeinem der Ansprüche 9 bis 14, welches kontinuierlich durchgeführt wird.

16. Verfahren gemäß irgendeinem der vorangehenden Ansprüche, worin das Alkenylbenzol ein 5-(o-Tolyl)-pent-2-en oder ein 5-(o-Tolyl)-pent-1-en ist.

17. Diskontinuierliches Verfahren gemäß Anspruch 1 zur Herstellung von 1,5-Dimethyltetrahydronaphthalin mittels Cyclisierung von 5-(o-Tolyl)-pent-2-en, welches die Schritte umfaßt, daß:

(a) ein aliquoter Teil des im wesentlichen reinen 5-(o-Tolyl)-pent-2-ens mit einer katalytisch wirksamen Menge eines festen Cyclisierungskatalysators, der eine im wesentlichen neutrale, ultrastabile Wasserstoff-Form eines kristallin Alumosilikat-Y-Zeoliths beinhaltet, welcher ein massenbezogenes Siliciumdioxid:Aluminiumoxid-Molverhältnis von mindestens 12:1 aufweist, im Gitter im Durchschnitt nicht mehr als 10 Brönsted-Säure-Zentren pro Elementarzelle aufweist, eine Elementarzellengröße von nicht mehr als 24,3 Angström aufweist und einen als elementares Natrium berechneten und auf das Gewicht des Y-Zeoliths bezogenen Natrium-Gehalt von nicht mehr als 0,4 Gew.-% aufweist, oder welcher ausgedrückt als massenbezogenes Natriumoxid:Aluminiumoxid-Molverhältnis im Bereich von 0,001:1 bis kleiner als 1:1 liegt, bei einer Temperatur im Bereich von 120 °C bis 350 °C und einem Druck, welcher ausreicht, und die Reaktanten während der Cyclisierung im wesentlichen im flüssigen Zustand zu halten, innerhalb eines Zeitraums, welcher ausreicht, um das 5-(o-Tolyl)-pent-2-en im wesentlichen in eine an 1,5-Dimethyltetrahydronaphthalin angereicherte flüssige Zusammensetzung umzuwandeln, in Berührung gebracht wird;

(b) zu diesem flüssigen Produkt ein weiterer aliquoter Teil des im wesentlichen reinen 5-(o-Tolyl)-pent-2-ens zugegeben wird, wobei die Temperatur und die Bedingungen, bei denen eine flüssige Phase vorliegt, konstant gehalten werden, und die Zugabe mit einer Geschwindigkeit erfolgt, welche eine Wärmeabfuhr und Kontrolle des besagten Temperaturbereichs erlaubt;

(c) diese Rückfluß-Temperatur-Bereiche konstant gehalten werden, wobei der Druck mit einer Geschwindigkeit vermindert wird, die zur Aufrechterhaltung dieses Rückfluß-Bereichs ausreicht, bis das 5-(o-Tolyl)-pent-2-en im wesentlichen in ein an 1,5-Dimethyltetrahydronaphthalin angereichertes



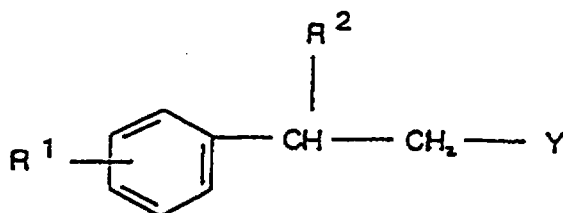
flüssiges Produkt umgewandelt ist; und

(d) aus diesem flüssigen Produkt mindestens etwa 70 Gew.-% des darin enthaltenen 1,5-Dimethyltetrahydronaphthalins mittels Flash-Destillation entfernt werden, worauf eine flüssige Rückstands-Zusammensetzung zurückbleibt.

18. Verfahren gemäß Anspruch 17, worin die Abfolge der Schritte (b), (c) und (d) mindestens einmal wiederholt wird.
19. Verfahren gemäß Anspruch 17 oder 18, worin im Anschluß an Schritt (d) die Rückstands-Zusammensetzung in der Reaktionszone durch Erhitzen dieser besagten Zusammensetzung auf eine Temperatur im Bereich von 180 °C bis 350 °C weiterverarbeitet wird, wobei ein Druck aufrechterhalten wird, der ausreicht, um diese Zusammensetzung im wesentlichen in flüssiger Phase zu halten, und das 1,5-Dimethyltetrahydronaphthalin gleichzeitig mittels Flash-Destillation aus der Reaktionszone entfernt wird.

15 Revendications

1. Procédé de cyclisation d'un alkénylbenzène de formule :



(I)

dans laquelle :

R¹ est de l'hydrogène, un groupe méthyle ou éthyle,

R² est de l'hydrogène ou un groupe méthyle, et

Y est -CH=CH-CH₃ ou -CH₂-CH=CH₂

qui consiste à mettre en contact ledit alkénylbenzène sous forme liquide avec un catalyseur de cyclisation solide constitué d'une forme hydrogénée ultrastable d'acidité relativement basse de zéolite d'aluminosilicate cristallin Y ayant un rapport molaire apparent de la silice à l'alumine d'au moins 12:1, une moyenne d'au maximum 10 sites acides de Bronsted dans l'ossature par unité cellulaire, une dimension de l'unité cellulaire qui ne dépasse pas 24,3 angstroms et une teneur en sodium qui ne dépasse pas 0,4 pour-cent en poids calculée en sodium élémentaire et sur base du poids de la zéolite, ou en termes de rapport molaire apparent de l'oxyde de sodium à l'alumine dans la plage de 0,001:1 à moins de 1:1, à une température de 120 à 350 °C et sous une pression suffisante pour maintenir les réactifs sensiblement à l'état liquide au cours de la cyclisation.

2. Procédé selon la revendication 1, dans lequel ladite température se situe dans la plage de 160 à 250 °C.
3. Procédé selon la revendication 1 ou 2, dans lequel ledit alkénylbenzène est cyclisé en présence de dialkyltétrahydronaphthalène préformé.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit catalyseur de zéolite est une poudre et ladite mise en contact se fait dans un réacteur à cuve agité.
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit catalyseur de zéolite est supporté sur un oxyde minéral réfractaire poreux.
6. Procédé selon la revendication 5, dans lequel ledit catalyseur de zéolite constitue 10 à 90 % en poids du poids total du catalyseur supporté.
7. Procédé selon l'une quelconque des revendications précédentes, mis en oeuvre en continu.



8. Procédé selon l'une quelconque des revendications 1 à 6, mis en oeuvre en discontinu.
9. Procédé selon l'une quelconque des revendications précédentes comprenant les stades suivants:
- (A) on forme initialement dans un réacteur à cuve agité une charge d'initiateur comprenant un hydrocarbure non réactif qui est en phase liquide à une température de 160 à 250 °C et sous une pression de 17 kPa à 3620 kPa (pression absolue de 2,5 à 525 livres par pouce carré), et un catalyseur de cyclisation pulvérulent constitué d'une forme hydrogénée ultrastable d'acidité relativement basse de zéolite d'aluminosilicate cristallin Y ayant un rapport molaire apparent de la silice à l'alumine d'au moins 12:1, une moyenne d'au maximum 10 sites acides de Bronsted dans l'ossature par unité cellulaire, une dimension de l'unité cellulaire qui ne dépasse pas 24,3 angstroms et une teneur en sodium qui ne dépasse pas 0,4 pour-cent en poids calculée en sodium élémentaire et sur base du poids de ladite zéolite, ou en termes de rapport molaire apparent de l'oxyde de sodium à l'alumine dans la plage de 0,001:1 à moins de 1:1, et
- (B) on ajoute à ladite charge d'initiateur dans ledit réacteur à cuve agité dans des conditions de phase liquide un alkénylbenzène de formule (I) tel que défini dans la revendication 1, ledit alkénylbenzène étant sensiblement exempt de composants non hydrocarbonés, et on met en contact ledit alkénylbenzène avec ledit catalyseur de zéolite à une température de 120 à 350 °C sous une pression suffisante pour maintenir les réactifs sensiblement à l'état liquide au cours de la cyclisation.
10. Procédé selon la revendication 9, dans lequel ledit hydrocarbure non réactif est constitué d'un alkyltétrahydronaphtalène.
11. Procédé selon la revendication 9 ou 10, dans lequel la concentration dudit catalyseur se situe dans la plage de 0,3 à 2 % en poids.
12. Procédé selon l'une quelconque des revendications 9 à 11, dans lequel l'alkyltétrahydro naphtalène produit est retiré dudit réacteur à cuve par distillation éclair en laissant subsister dans ledit réacteur à cuve une composition résiduaire comprenant ledit catalyseur de zéolite, des dialkyltétrahydro naphtalènes résiduaire et des sous-produits hydrocarbonés ayant des poids moléculaires supérieurs à celui desdits dialkyltétrahydronaphtalènes résiduaire.
13. Procédé selon la revendication 12, dans lequel, ensuite, une quantité supplémentaire d'alkénylbenzène est ajoutée à ladite composition résiduaire, ledit alkénylbenzène sous forme liquide est mis en contact avec ledit catalyseur de zéolite à une température de 120 à 350 °C pendant une période suffisante pour obtenir un produit liquide enrichi en ledit alkyltétrahydronaphtalène, après quoi ladite distillation éclair est répétée.
14. Procédé selon la revendication 12, dans lequel ladite composition résiduaire dudit réacteur à cuve est chauffée à une température de 180 à 350 °C sous une pression suffisante pour maintenir ladite composition résiduaire sensiblement en phase liquide, en sorte de craquer ladite composition et de former du diméthyltétrahydronaphtalène qui est simultanément retiré dudit réacteur à cuve par distillation éclair.
15. Procédé selon l'une quelconque des revendications 9 à 14, mis en oeuvre en continu.
16. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit alkylbenzène est un 5-(O-tolyl)pent-2-ène ou un 5-(O-tolyl)-pent-1-ène.
17. Procédé discontinu selon la revendication 1 pour préparer du 1,5-diméthyltétrahydronaphtalène par cyclisation de 5-(O-tolyl)-pent-2-ène comprenant les stades suivants :
- (a) on met en contact une fraction aliquote de 5-(O-tolyl)-pent-2-ène sensiblement pur avec une quantité catalytiquement efficace d'un catalyseur de cyclisation solide constitué d'une forme hydrogénée ultrastable sensiblement neutre de zéolite d'aluminosilicate cristallin Y ayant un rapport molaire apparent de la silice à l'alumine d'au moins 12:1, une moyenne d'au maximum 10 sites acides de Bronsted dans l'ossature par unité cellulaire, une dimension de l'unité cellulaire qui ne dépasse pas 24,3 angstroms et une teneur en sodium qui ne dépasse pas 0,4 pour-cent en poids calculée en sodium élémentaire et sur base du poids de ladite zéolite Y, ou en termes de rapport



5 molaire apparent de l'oxyde de sodium à l'alumine dans la plage de 0,001:1 à moins de 1:1, à une température de 120 à 350 ° C sous une pression suffisante pour maintenir les réactifs sensiblement à l'état liquide au cours de la cyclisation et pendant une période de temps suffisante pour convertir sensiblement ledit 5-(O-tolyl)-pent-2-ène en une composition liquide enrichie en 1,5-diméthyltétrahydronaphtalène,

(b) on ajoute audit produit liquide une autre fraction aliquote de 5-(O-tolyl)-pent-2-ène sensiblement pur en maintenant ladite température et lesdites conditions de phase liquide, ladite addition étant effectuée selon un débit qui permet l'élimination de la chaleur et le réglage de ladite plage de températures,

10 (c) on maintient lesdits niveaux de température de reflux en réduisant la pression à une cadence suffisante pour maintenir ledit niveau de reflux jusqu'à ce que ledit 5-(O-tolyl)-pent-2-ène soit sensiblement converti en un produit liquide enrichi en 1,5-diméthyltétrahydronaphtalène, et

(d) on sépare par distillation éclair dudit produit liquide au moins environ 70 % en poids dudit 1,5-diméthyltétrahydronaphtalène qui s'y trouve, en laissant subsister une composition liquide résiduaire.

15 18. Procédé selon la revendication 17, dans lequel la séquence des stades (b), (c) et (d) est répétée au moins une fois.

20 19. Procédé selon la revendication 17 ou 18, dans lequel, après le stade (d), ladite composition résiduaire de ladite zone réactionnelle est encore traitée par chauffage de ladite composition à une température de 180 à 350 ° C en maintenant une pression suffisante pour maintenir ladite composition sensiblement en phase liquide et en retirant simultanément de ladite zone réactionnelle par distillation éclair du 1,5-diméthyltétrahydronaphtalène.