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(54) Titre : PROCEDE POUR L'ALKYLATION DE MONO-ALKYLATS LOURDS D'HYDROCARBURES AROMATIQUES MONOCYCLIQUES

(54) Title: PROCESS FOR THE ALKYLATION OF HEAVY MONO-ALKYLATES OF SINGLE-RING AROMATIC HYDROCARBONS

(57) Abrégé/Abstract:
A heavy mono-alkylated benzene, having a heavy-alkylate content of at least 20 weight percent, is produced by reacting a heavy mono-alkylated benzene with an olefin, having from 6 to 14 carbon atoms, at a pressure of up to about 10 bars and a temperature of about from 100° to 225° C in the presence of an acidic catalyst. The acidic catalyst can be a molecular sieve or clay. The molecular sieve can be a natural or synthetic zeolite.

ABSTRACT

A heavy mono-alkylated benzene, having a heavy-alkylate content of at least 20 weight percent, is produced by reacting a heavy mono-alkylated benzene with an olefin, having from 6 to 14 carbon atoms, at a pressure of up to about 10 bars and a temperature of about from 100° to 225° C in the presence of an acidic catalyst. The acidic catalyst can be a molecular sieve or clay. The molecular sieve can be a natural or synthetic zeolite.

PROCESS FOR THE ALKYLATION OF HEAVY MONO-ALKYLATES OF SINGLE-RING AROMATIC HYDROCARBONS

The present invention relates to a process for the alkylation of heavy mono-alkylates of single-ring aromatic hydrocarbons to produce an alkylate with a high heavy-alkylate content.

BACKGROUND OF THE INVENTION

The alkylation of aromatics with a variety of Lewis or Brönsted acid catalysts is well known. Typical commercial catalysts include phosphoric acid/kieselguhr, aluminum chloride, and hydrogen fluoride. Alkylation with lower molecular weight olefins, such as propylene, can be carried out in the liquid or vapor phase. For alkylations with higher olefins, such as C_{16+} olefins, the alkylations are done in the liquid phase, usually in the presence of hydrogen fluoride. Alkylations of benzene with higher olefins is especially difficult, and requires hydrogen fluoride treatment. Such a process is disclosed by Himes in U.S. Patent No. 4,503,277, entitled "HF Regeneration in Aromatic Hydrocarbon Alkylation Process". However, hydrogen fluoride is not environmentally attractive.

Alkylates derived from heavy olefin feeds (olefins having at least sixteen carbon atoms) used in the manufacturing of lubrication oil sulfonates and as carrier fluids typically contain some amount (5 to 15%) of heavy-alkylate species. For certain functions, it is desirable to maximize this heavy-alkylate content for performance reasons, however increasing the heavy-alkylate content above 20 weight percent is not a trivial task, because the conditions that favor di-alkylation usually favors the formation of large amounts of very high molecular weight olefin oligomers.

U.S. Patent No. 4,148,834, entitled "Preparation of Synthetic Hydraulic Lubricants," discloses the production of dialkylaromatic hydrocarbons from aromatic hydrocarbons by first reacting from one to fifteen moles of aromatic hydrocarbon with one mole of a C_6-C_{18} linear monoolefin at a temperature of from 5 to 100° C in the presence of from one to thirty moles HF per mole of

aromatic hydrocarbon, then recovering the monoalkylaromatic from the reaction mixture and then reacting from one to ten moles of the monoalkylaromatic with one mole of linear C_6-C_{18} mono-olefin at a temperature of from 60° to 90°C in the presence of from 2 to 10 weight %, based on the olefin, of AlC_{l3} or $AlBr_3$, and recovering the dialkylaromatic hydrocarbons from the reaction mixture.

SUMMARY OF THE INVENTION

The present invention provides a process for increasing the heavy-alkylate content of heavy mono-alkylates to at least 20 weight percent, preferably at least 50 weight percent, heavy-alkylate. The process comprises reacting a heavy mono-alkylated single-ring aromatic hydrocarbon with an olefin having from 6 to 14 carbon atoms at a pressure of up to about 10 bars and a temperature of about from 100° to 225°C in the presence of an acidic catalyst. The acidic catalyst can be a clay or a molecular sieve (such as a natural or synthetic zeolite).

Preferably, the single-ring aromatic hydrocarbon that is alkylated is benzene, toluene, cumene, xylene, or a mixture thereof. Most preferably, the single-ring aromatic hydrocarbon is benzene.

Preferably, the alkyl group of the mono-alkylated single-ring aromatic hydrocarbon has from 20 to 28 carbon atoms, and the mono-alkylate content of the mono-alkylated single-ring aromatic hydrocarbon is at least 88 weight percent.

According to one aspect of the present invention, there is provided a process for increasing the heavy-alkylate content of a heavy mono-alkylated single-ring aromatic hydrocarbon to at least 20 weight percent, said process comprising reacting said heavy mono-alkylated single-ring aromatic hydrocarbon with an olefin having from 6 to 14 carbon atoms at a pressure of up to about 10 bars and a temperature of about from 100° to 225°C in the presence of an acidic catalyst selected from the group consisting of molecular sieves and

clays.

According to another aspect of the present invention, there is provided a process for increasing the heavy-alkylate content of a heavy benzene mono-alkylate to at least 50 weight percent, the process comprising reacting the heavy benzene mono-alkylate with an olefin having from 6 to 14 carbon atoms at a pressure of about from 0 to 10 bars and a temperature of about from 100° to 225° C in the presence of an acidic clay catalyst, wherein the mono-alkylate content of the initial mono-alkylated benzene is at least 80 weight percent, and wherein the alkyl group of the mono-alkylated benzene has from 20 to 28 carbon atoms.

DETAILED DESCRIPTION OF THE INVENTION

In its broadest aspect, the present invention involves a process for producing an alkylated single-ring aromatic hydrocarbon having a heavy-alkylate content of at least 20 weight percent, preferably at least 50 weight percent.

By “heavy-alkylate”, we mean the amount of total alkylate that is comprised of those chemical species present with molecular weights higher than that of the mono-alkylate. These chemical species present with molecular weights higher than that of the mono-alkylate may be composed of, but are not limited to:

(a) mono-alkylated aromatics of oligomerized olefins,
(b) di-alkylated aromatic species,
(c) tri-alkylated aromatic species, and
(d) oligomerized olefins species.

HEAVY MONO-ALKYLATED SINGLE-RING AROMATIC HYDROCARBON

In the present invention, a "heavy mono-alkylated single-ring aromatic hydrocarbon" is reacted with an olefin under certain conditions to produce an alkylate with a high heavy-alkylate content.

By the phrase "heavy mono-alkylated single-ring aromatic hydrocarbon," we mean an aromatic hydrocarbon containing a single aromatic ring and having attached to that single aromatic ring a single long-chain alkyl group having at least sixteen carbon atoms. Preferably, the long-chain alkyl group is derived from normal alpha olefins, but it can contain some degree of branching. Preferably, the long-chain alkyl group has from 20 to 28 carbon atoms.

The single-ring aromatic hydrocarbon that is alkylated is preferably benzene, toluene, cumene, xylene, or mixtures thereof. The "alkyl group" refers to the long-chained alkyl group attached by alkylation, and not to any methyl group or groups. We do not consider methyl groups to be long-chain.

Preferably, the mono-alkylate content of the mono-alkylated single-ring aromatic hydrocarbon is at least 88 weight percent. By "mono-alkylate content," we mean the amount of alkylated single-ring aromatic hydrocarbon that only has one long-chain alkyl group. The remainder could consist of minor amounts of di-alkylated single-ring aromatic hydrocarbons, tri-alkylated single-ring aromatic hydrocarbons, oligomerized olefins, and alkylates formed from oligomerized olefins.

The alkylated single-ring aromatic hydrocarbon can be formed by any conventional process, such as processes similar to those disclosed by Resh in U.S. Patent No. 4,691,098 entitled "Process for Production of Alkyl Aromatics," and disclosed by Kocal in U.S. Patent No. 5,334,793 entitled "Increasing

Catalyst Life and Improving Product Linearity in the Alkylation of Aromatics with Linear Olefins."

OLEFIN

In the present invention, a heavy mono-alkylated single-ring aromatic hydrocarbon is reacted with an olefin having from 6 to 14 carbon atoms. Preferably, the olefin is a normal alpha olefin, but the olefin can contain some degree of branching.

CATALYST

The catalyst of the present invention is a solid, acidic catalyst, such as a molecular sieve or clay. Preferred molecular sieves include natural and synthetic zeolites.

Preferably, the acidic catalyst comprises the acid forms of an acidic clay, or an acidic molecular sieve (such as a zeolite) having a pore size of at least 6.0 Angstroms. Such zeolites include zeolite Y, beta, SSZ-25, SSZ-26, and SSZ-33. Other possible catalysts include L zeolite, mordenite, boggsite, cloverite, VPI-5, MCM-41, MCM-36, SAPO-8, SAPO-5, MAPO-36, SAPO-40, SAPO-41, MAPSO-46, CoAPO-50, hexagonal faujasite (EMC-2), gmelinite, mazzite (omega zeolite), offretite, ZSM-18, and ZSM-12. These catalysts are discussed in Rosemarie Szostak's *Handbook of Molecular Sieves* (New York, Van Nostrand Reinhold, 1992). The catalyst is activated prior to use. Preferably, the activated catalyst is used without exposure to atmospheric water. Most preferably, the acidic catalyst is an acidic clay.

Useful acidic clays may be derived from naturally occurring or synthetic materials. One skilled in the art would realize that there are a number of such clays that are known to be alkylation catalysts. Examples of such acidic clays include montmorillonite, laponite, and saponite. Pillared clays may also be used as catalysts.

PROCESS CONDITIONS

The alkylation reaction is typically carried out with a heavy mono-alkylated single-ring aromatic hydrocarbon and an olefin in molar ratios of about from 1:15 to 25:1. The process is typically carried out at a pressure of up to about 10 bars and a temperature of about from 100° to 225° C in the presence of an acidic catalyst. The process can be operated using catalysts in either a batch or fixed bed reactor. As the olefin has a low boiling point, the process is preferably carried out in the liquid phase. The alkylation process may be carried out in batch or continuous mode. In the batch mode a typical method is to use a stirred autoclave or glass flask which may be heated to the desired reaction temperature. A continuous process is most efficiently carried out in a fixed bed process. Space rates in a fixed bed process can be in the range of about from 0.01 to 10 or more weight hourly space velocity (WHSV).

In a fixed bed process the catalyst is charged to the reactor and activated or dried at a temperature of at least 100°C under flowing inert, dry gas. After activation, the catalyst is cooled to ambient temperature and a flow of the heavy mono-alkylated single-ring aromatic hydrocarbon is introduced. Pressure is increased by means of a back pressure valve so that the pressure is above the bubble point pressure of the aromatic species at the desired reaction temperature. After pressurizing the system to the desired pressure, the temperature is increased to the desired reaction temperature. A flow of the olefin is then mixed with the heavy mono-alkylated single-ring aromatic hydrocarbon and is allowed to flow over the catalyst. The reactor effluent containing dialkylate product and excess aromatic is collected. Excess olefin is then removed by distillation, stripping, evaporation under vacuum, or other means known to those skilled in the art .

EXAMPLES

The invention will be further illustrated by following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

Unless stated otherwise, all percentages in the Examples are weight percentages.

EXAMPLE 1

A commercial acidic zeolite Y extrudate catalyst available from Aldrich Chemical Company (1.85 grams) was weighed into a 30 cc glass serum bottle. The bottle was then placed in an oven at 100° C in air for approximately 17 hours. The bottle was then removed from the oven and immediately sealed with a TEFLON rubber faced septum using a crimpon tool. After the bottle had cooled to room temperature, 2 ml of a C_{20-24} NAO alkyl benzene alkylate (consisting of 88 % mono-alkylate and 12 % heavy alkylate by Supercritical Fluid Chromatography (SFC)) and 5 ml of 1-decene were added to the vial via syringe. The bottle was then placed in an oil bath maintained at between 145° C and 155° C. After 24 hours, the bottle was removed and allowed to cool to room temperature and then the bottle was opened and the contents were gravity filtered through filter paper to afford a liquid product. Analysis of this liquid by SFC showed the following composition: 31 % 1-decene dimer; 53 % mono-alkylate and 16 % heavy-alkylate. The ratio of mono-alkylate to heavy alkylate in this product is 77:23. In other words, the heavy-alkylate content of the total alkylate product was 23 %.

EXAMPLE 2

To a 30 cc glass serum bottle was added 1.85 grams of Filtrol F-24 acid clay catalyst granules (available from Englehard Corporation, Elyria, Ohio). The bottle was then placed in an oven at 100°C in air for approximately 17 hours. The bottle was then removed from the oven and immediately sealed with a TEFLON rubber faced septum using a crimpon tool. After the bottle had cooled to room temperature, 2 ml of a C_{20-24} NAO alkyl benzene alkylate (consisting of 88 % mono-alkylate and 12 % heavy alkylate by SFC) and 5 ml of 1-decene were added to the vial via syringe. The bottle was then placed in an oil bath maintained at between 145° C and 155° C. After 24 hours, the bottle was removed and allowed to cool to room temperature and then the bottle was opened and the contents were gravity filtered through filter paper to afford a liquid product. Analysis of this liquid by SFC showed the following composition: 11 % 1-decene dimer; 25 % mono-alkylate and 64 % heavy alkylate. The ratio of

mono-alkylate to heavy-alkylate is 15:85. In other words, the heavy-alkylate content of the total alkylate product was 85 %.

EXAMPLE 3

To a 30 cc glass serum bottle was added 1.85 grams of Filtrol F-24 acid clay catalyst granules (available from Engelhard Corporation, Elyria, Ohio). The bottle was then placed in an oven at 100° C in air for approximately 17 hours. The bottle was then removed from the oven and immediately sealed with a TEFLON rubber faced septum using a crimpon tool. After the bottle had cooled to room temperature, 2 ml of a C_{18} NAO alkyl benzene product (consisting of approximately 82 % mono-alkylate and 18 % heavy alkylate by SFC) and 5 ml of 1-decene were added to the vial via syringe. The bottle was then placed in an oil bath maintained at between 145° C and 155° C. After 24 hours, the bottle was removed and allowed to cool to room temperature and then the bottle was opened and the contents were gravity filtered through filter paper to afford a liquid product. Analysis of this liquid by SFC showed the following composition: 15 % 1-decene dimer; 23 % mono-alkylate and 62 % heavy alkylate. The ratio of mono-alkylate to heavy-alkylate is 27:73. In other words, the heavy-alkylate content of the total alkylate product was 73 %.

Analysis of this product by Gas Chromatography-Mass Spectroscopy (GCMS) confirmed the 1-decene dimer assignment and also showed that the mono-alkylate to be composed of approximately a 50:50 mixture of C_{18} NAO benzene mono-alkylate and 1-decene trimer. The heavy-alkylate was shown by GCMS to be composed of benzene substituted with C_{28} and C_{38} alkyl groups consistent with the addition of one and two 1-decene groups onto the aromatic ring, of the starting mono-alkylate, respectively.

Procedure for Determining Composition of Alkylated Heavy Alkylates by Supercritical Fluid Chromatography (SFC)

A Dionex, Lee Scientific Model 600 Supercritical Fluid Chromatograph (SFC) equipped with a 10 meter x 195 micron OD/50 micron ID, 0.25 micron film (SB-Methyl-100) capillary column, and FID detector operating at 325° C and carbon

dioxide eluent was used with split injection. The following density ramp program was used (isothermal oven at 100° C):

Initial Density = 0.2 g/cc
Inject Sample
Hold five minutes
Ramp to 0.3 g/cc at 0.02 g/cc/min
Ramp to 0.5 g/cc at 0.01 g/cc/min
Ramp to 0.76 g/cc at 0.02 g/cc/min
Hold twelve minutes

For the benzene alkylates studied and under the conditions that contribute to the relative retention times (carrier gas flow, condition of the column, and other factors), the 1-decene dimer eluted between 21 and 26 minutes, the C_{18} NAO benzene mono-alkylate eluted between 27 and 32,5 minutes, the C_{18} NAO benzene heavy-alkylate eluted between 33 and 43 minutes, the C_{20-24} NAO benzene mono-alkylate eluted between 28 and 34 minutes, the C_{20-24} NAO heavy-alkylate eluted between 34.5 and 45 minutes.

The composition of the products were calculated as follows:

$$\text{Percent decene Dimer} = \frac{\text{Peak Area between 21 and 26 minutes}}{\text{Peak Area between 20 and 45 minutes}} \times 100$$

$$\text{Percent } C_{18} \text{ NAO Benzene Mono-Alkylate} = \frac{\text{Peak Area between 27 and 32.5 minutes}}{\text{Peak Area between 20 and 45 minutes}} \times 100$$

$$\text{Percent } C_{18} \text{ NAO Benzene Heavy-Alkylate} = \frac{\text{Peak Area between 33 and 43 minutes}}{\text{Peak Area between 20 and 45 minutes}} \times 100$$

$$\text{Percent } C_{20-24} \text{ NAO Benzene Mono-Alkylate} = \frac{\text{Peak Area between 28 and 34 minutes}}{\text{Peak Area between 20 and 45 minutes}} \times 100$$

$$\text{Benzene Heavy-Alkylate} = \frac{\text{Percent } C_{20\text{-}24} \text{ NAO Peak Area between 34.5 and 45 minutes}}{\text{Peak Area between 20 and 45 minutes}} \times 100$$

Procedure for Determining the Number Average Molecular Weight (Mn), Weight Average Molecular Weight (Mw) and Heavy-Alkylate Content By Size Exclusion Chromatography (SEC)

The chromatographic system used to determine Mn, Mw and Heavy-alkylate Content consisted of the following:

Waters model M 510 HPLC pump
Rheodyne model 71-25 injection valve fitted with a 10 µl injection loop
SEC column (stainless steel, 60 cm x 7mm ID) filled with polystyrene divinylbenzene PL Gel (10 micron size, 100 Angstrom porosity from Touzard and Matignon)
Waters model 410 differential refractomer detector
Shimadzu-Chromatopac C-R3 integrator

The mobile phase used was HPLC grade tetrahydrofuran (THF) degassed with helium and stored under helium. The chormatographic conditions used were: THF flow = 1.0 ml/min; Column temperature = 25° C, Detector Temperature 34° C, Column pressure (maximum) = 1500 psi.

The column was calibrated using polystyrene standards as follows:

Time (Minutes)	Molecular Weight
11.905	834
12.438	582
13.087	386
13.336	358
13.468	330
13.934	274
14.234	246
17.110	92 (Toluene)

The sample to be analyzed (0.1 gm) was dissolved in 0.02 gm toluene and 1.5 ml THF. The amount of sample injected onto the SEC column was 0.67 gm. Quantitative analysis of the chromatogram was performed by the integrator using toluene as an internal retention time calibration standard.

COMPARATIVE EXAMPLE A

A flow alkylation reactor operated under various conditions was used to alkylate a C_{20-24} NAO benzene alkylate (composed of 90 % mono-alkylate and 10 % heavy alkylate by SEC) with 1-octene. Following reaction, the products were distilled to remove the HF catalyst. The products were then analyzed by SEC. The different reactor conditions and products obtained are summarized in the following table.

Sample=>	Feed	1	2	3	4	5
REACTOR CONDITIONS						
Reactor Temperature (°C)		35	50	50	50	65
HF/C_8 CMR		2	2	1	4	4
C_{20-24} Alkylate/C_8 CMR		2	2	2	2	2
HF Flow (cc/min)		16.0	16.0	9.0	26.0	26.0
C_{20-24} Alkylate Flow (cc/min)		53.0	53.0	59.0	44.0	44.0
C_8 Flow (cc/min)		8.0	8.0	9.0	7.0	7.0
PRODUCT COMPOSITION						
Molecular Weight (Number Ave.)	383	365	369	371	368	370
Molecular Weight (Weight Ave.)	408	401	404	404	402	403
Heavy-alkylate content (wt. %)	10.2	10.9	10.9	11.3	10.6	10.7

This comparative example shows that further alkylation using an HF catalyst does not cause a significant increase in heavy-alkylate content.

While the present invention has been described with reference to specific embodiments, this application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

What is claimed is:

1. A process for increasing the heavy-alkylate content of a heavy mono-alkylated single-ring aromatic hydrocarbon to at least 20 weight percent, said process comprising reacting said heavy mono-alkylated single-ring aromatic hydrocarbon with an olefin having from 6 to 14 carbon atoms at a pressure of up to about 10 bars and a temperature of about from 100° to 225° C in the presence of an acidic catalyst selected from the group consisting of molecular sieves and clays.

2. A process according to Claim 1 wherein said molecular sieve is selected from the group consisting of natural zeolites and synthetic zeolites.

3. A process according to Claim 1 wherein the reaction product of said process has a heavy-alkylate content of at least 50 weight percent.

4. A process according to Claim 1 wherein said heavy mono-alkylated single-ring aromatic hydrocarbon is formed by the alkylation of a single-ring aromatic hydrocarbon selected from the group consisting of benzene, toluene, cumene, xylene, and mixtures thereof.

5. A process according to Claim 4 wherein said heavy mono-alkylated single-ring aromatic hydrocarbon is formed by the alkylation of benzene.

6. A process according to Claim 1 wherein the alkyl group of the mono-alkylated single-ring aromatic hydrocarbon has from 20 to 28 carbon atoms.

7. A process according to Claim 1 wherein the alkyl group of the mono-alkylated single-ring aromatic hydrocarbon has from 20 to 28 carbon atoms, and wherein the mono-alkylate content of the initial mono-alkylated single-ring aromatic hydrocarbon is at least 80 weight percent.

8. A process according to Claim 1 wherein said acidic catalyst is an acidic clay.

9. A product produced by the process according to any one of Claims 1, 2 and 4 to 8.

10. A process for increasing the heavy-alkylate content of a heavy benzene mono-alkylate to at least 50 weight percent, said process comprising reacting the heavy benzene mono-alkylate with an olefin having from 6 to 14 carbon atoms at a pressure of about from 0 to 10 bars and a temperature of about from 100° to 225° C in the presence of an acidic clay catalyst, wherein the mono-alkylate content of the initial mono-alkylated benzene is at least 80 weight percent, and wherein the alkyl group of the mono-alkylated benzene has from 20 to 28 carbon atoms.

11. An alkylated single-ring aromatic hydrocarbon having a heavy-alkylate content of at least 50 weight percent produced by the process of any one of claims 1, 2, 4 to 8 and 10.