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3,442,964

PRODUCTION OF DETERGENT ALKYLATE

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No Drawing. Filed Jan. 12, 1965, Ser. No. 425,059

Claims priority, application Great Britain, Jan. 17, 1964, 2,197/64

Int. Cl. C07c 3/52, 15/00, 143/24

U.S. Cl. 260—671

19 Claims 10

ABSTRACT OF THE DISCLOSURE

Detergent alkylates are prepared by the alkylation of aromatic hydrocarbons with C_{10} – C_{16} olefins. The olefins are prepared by dimerizing C_5 – C_8 olefins with a catalyst comprised of a synthetic petroleum cracking catalyst and a stable salt of a transition metal.

The present invention relates to the production of detergent alkylate.

The preparation of detergent alkylate fractions having an alkyl chain length of about C_{10} to C_{16} which give alkylbenzene sulphonate detergents, which can be readily metabolised by sewage bacteria, has recently assumed considerable importance. Hitherto, it has been thought that the use of straight chain alkylbenzenes was necessary to give biologically degradable alkylbenzene sulphonates, in contrast to the conventional highly branched-chain alkylbenzene sulphonates, derived for instance from propylene tetramer.

It has now been discovered that detergent alkylate fractions can be produced, which give biologically degradable alkylbenzene sulphonates, but which do not consist predominantly of straight chain alkylbenzenes.

According to the present invention a process for the production of detergent alkylate comprises dimerising in the liquid phase straight chain monoolefines in the C_5 to C_8 carbon number range in the presence of a catalyst comprising a synthetic petroleum cracking catalyst and a salt of a transition metal, which is heat stable under catalyst activation and regeneration conditions, and alkylating with a fraction of the dimerisation product in the C_{10} to C_{16} carbon number range an aromatic hydrocarbon in the presence of an alkylation catalyst.

Benzene is the preferred aromatic hydrocarbon.

The starting materials for the process of the present invention are straight chain monoolefines having carbon numbers in the range C_5 – C_8 . The feedstock may be obtained in any suitable manner, for instance as a fraction of the products of thermally cracking a high molecular weight paraffinic hydrocarbon, preferably after purification of the cracked fraction to remove sulphur compounds, diolefines and acetylenic hydrocarbons. Other suitable feedstocks are obtained by polymerisation of lower olefines, especially ethylene, propylene or butene and isolation of a fraction from the polymer consisting of straight chain monoolefines having 5 to 8 carbon atoms. Suitable fractions can also be made by dehydrogenation of C_5 to C_8 normal paraffins. In this case the olefine-paraffin mixture from the dehydrogenation may be used as feedstock, and unreacted olefine and paraffin recycled in part to the dimerisation and in part to the dehydrogenation. The position of the double bond in the molecule is not critical, but the starting material should not contain an appreciable proportion of branched chain olefines. The presence of saturated hydrocarbons in the feedstock can be tolerated, since these do not materially affect the dimerisation step; it is however preferred to use feedstocks

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not containing substantial amounts of such hydrocarbons particularly if it is desired to recycle monomeric olefine separated from the dimerisation product. Small amounts of aromatic hydrocarbons can be tolerated in the feedstock, but the proportion must be small, since these tend to form undesirable alkylated aromatics by reaction with olefine in the feed. Aromatic free feedstocks are generally to be preferred. It is preferred to operate at relatively low olefine conversion per pass, and to recycle recovered monomer, since this gives higher yields of the required detergent olefine fraction. The flow rate of ethylene may conveniently be between 0.1 and 10 volumes of liquid olefine per volume of catalyst per hour.

The catalysts which may be used in the process of the invention comprise synthetic cracking catalysts used in the cracking of petroleum and a salt of a transition metal which is heat-stable under catalyst activation and regeneration conditions. Typical examples of the cracking catalysts are silica/alumina, silica/magnesia, silica/zirconia, silica/boria, and silica/titania catalysts. The preferred cracking catalyst is silica/alumina, suitably containing from 70 to 90% and preferably about 85% by weight of silica, although the proportion of silica to alumina may vary within moderately wide limits. The dimerisation catalyst may be suitably produced by impregnation of the cracking catalyst with a salt of a transition metal which does not decompose on heating with the formation of the oxide or the metal and removal of the acid radical (chloride, bromide sulphate etc.) from combination with the metal. Suitable salts include the halides and sulphates of nickel, cobalt, manganese and chromium or mixtures of any of these salts but the fluorides and iodides are less satisfactory. It is particularly preferred to impregnate the cracking catalyst with the chlorides of nickel, cobalt or manganese. The impregnation of the cracking catalyst is conveniently carried out with a solution of the transition metal salt in an ionising solvent, such as water. The catalyst is then preferably activated initially by heating in inert gas, nitrogen or air to temperatures in the range 350 to 850° C. The air or nitrogen used should be dry, and for catalysts impregnated with sulphates the use of air for activation is preferred.

Transition metal salts may be introduced into the cracking catalyst by other means than impregnation with a solution of a transition metal salt. Mixtures of transition metal sulphide and the cracking catalyst may be heated in the presence of free oxygen to oxidise the sulphide to sulphate. Thus nickel sulphate catalysts may be obtained from cracking catalyst containing nickel sulphide.

Transition metal halides may be introduced into the cracking by treating synthetic silica/alumina cracking catalyst comprising a transition metal or a transition metal oxide with a halogenating agent. Thus nickel chloride catalysts may be prepared by heating nickel or nickel oxide containing cracking catalysts with chlorine, hydrogen chloride, or ammonium chloride.

It has been found that the incorporation of the transition metal salt increases the selectivity of the catalyst for the production of dimers. The activity of the catalyst tends to decline with long continued use, owing largely to the deposition of carbon on the catalyst surface, and may be restored in the conventional way, for instance by heating the catalyst in oxygen containing gases to temperatures in the range 300° to 600° C. However, the selectivity of the catalyst for the dimerisation reaction remains at a high level.

The required C_{10} to C_{16} olefine fraction is suitably recovered from the dimerisation product by fractional distillation, preferably under reduced pressure. The C_5 to C_8 olefines contained in the dimerisation product can be sep-

arated and recycled to the dimerisation step since no significant skeletal isomerisation occurs during the dimerisation. The products of the dimerisation step are mostly olefines containing two or more branch chains, with only a small proportion of singly branched or normal olefines, such as n-dodecene. The production of biologically degradable alkylbenzene sulphonates from these products is therefore surprising.

The recovered C₁₀ to C₁₆ olefine fraction is condensed preferably with benzene in the presence of a suitable alkylation catalyst, such as aluminum chloride or anhydrous hydrogen fluoride. The use of anhydrous hydrogen fluoride is preferred. The condensation is suitably carried out in the liquid phase at a temperature in the range of about -20° C. to +100° C.

The alkylation product, after separation of the catalyst, is suitably fractionated to recover unreacted benzene for recycle, a small light alkylate fraction, and a distillate detergent alkylate fraction, leaving a small residue of heavy alkylate.

Example 1

A silica-alumina cracking catalyst containing 13% by weight of alumina was heated in air at 550° C., allowed to cool and heated with an aqueous solution of nickel chloride. After standing, excess solution was removed from the solid, which was then dried in air at 80° C. to give a product containing nickel chloride equivalent to 2.4% by weight of nickel in the solid. This dried catalyst was charged to a tubular reactor, through which air was passed at 550° C. After this treatment the air was replaced with nitrogen and the catalyst allowed to cool to the reaction temperature.

A hexene feedstock containing 40% of hexene-1 and 60% of hexene-2 plus hexene-3 was then pumped over the catalyst at a temperature of 80-90° C., a pressure of 400 p.s.i.g. and at a rate of 1 liquid volume per volume of catalyst per hour. The product was collected and fractionated to recover unpolymerised hexenes and a hexene-free polymer. The recovered hexenes amounted to 89.9% of the total liquid product and contained 4% of hexene-1 and 96% of hexene-2 plus hexene-3. The hexene-free polymer contained 91% of C₁₂ olefines, the remainder being high polymer (mainly C₁₈).

After this reaction the catalyst was regenerated by passing a current of air over the catalyst at 550° C., the air then being replaced by nitrogen and the catalyst cooled to reaction temperature. A hexene feedstock containing 29% of hexene-1 and 71% of hexene-2 plus hexene-3 was then processed over the regenerated catalyst under the same conditions as before, the product from this test containing 87.9% of unpolymerised hexenes (again containing 96% hexene-2 plus hexene-3 and 4% of hexene-1) and 13.1 wt. percent of C₁₂ and higher olefines, of which 91.5 percent was C₁₂ olefines. The C₁₂ product contained only traces of normal dodecene, less than 10% of methylundecene, and was largely dimethyldecenes, methyllethylnonenes and dimethyloctenes.

The C₁₂ olefine fraction from this second test was reacted with benzene, using 20 moles of benzene to 1 mole of olefine, with 20 moles of anhydrous hydrogen fluoride as catalyst, this alkylation reaction being carried out at 10-15° C. in the liquid phase. The HF catalyst layer was separated and the hydrocarbon layer washed with aqueous potassium hydroxide and water. After drying, the hydrocarbon product was fractionated to separate unreacted benzene, a very small light alkylate fraction, and a distillate detergent alkylate (recovered under reduced pressure) of boiling range 255-298.5° C./760 mm. A small residue of heavy alkylate remained. The yield of detergent alkylate was 130 parts by weight per 100 parts of this olefine consumed, and this product was 98.3% sulphonatable. The sodium salt of the sulphonic acid derived from this detergent alkylate degraded much more rapidly and completely in biological degradation tests than the sul-

phonate derived from conventional tetrapropylene benzene alkylate.

Example 2

This example shows the preparation of dimer suitable for the preparation of detergent alkylate and illustrates the operation of the C₆ dimerisation step with three different catalysts, containing nickel, manganese, and cobalt chlorides respectively. A silica-alumina cracking catalyst containing 13% of alumina which had been heated in air for 16 hours at 550° C. prior to use was employed as catalyst base. This base was impregnated with an aqueous solution of the metallic chloride as described in Example 1 to give in each case 10% by weight of the chloride on the dry catalyst. Each of the catalysts was then charged to a tubular reactor and activated by heating in a stream of nitrogen at 450° C. for 16 hours. Hexene-1 was then pumped over each catalyst at a temperature of 63° C. in the liquid phase, and the product recovered and separated into unpolymerised C₆ to C₁₂ and higher polymers. The conversions and yields obtained are shown in the following table.

	Nickel chloride catalyst		Manganese chloride catalyst		Cobalt chloride catalyst	
Olefine feed rate, vol- umes/volume cat./ hour.....	2.0	1.0	2.0	1.0	2.0	1.0
Conversion of hexene to total polymer.....	17	28	15	20	16.5	24
C ₁₂ olefine content of total polymer over C ₆	89	89	90	86.5	91	91.5

The C₁₂ fraction of the dimerisation product was suitable for condensation with benzene in the presence of an alkylation catalyst to produce detergent alkylate.

I claim:

1. A process for production of C₁₀ to C₁₆ olefins having two or more branches which comprises dimerizing in the liquid phase straight chain C₅ to C₈ monoolefins in the presence of a catalyst comprising a synthetic petroleum cracking catalyst and at least one salt of a transition metal, the salt being heat stable under catalyst activation and regeneration conditions, and recovering the C₁₀ to C₁₆ olefins formed.

2. A process as claimed in claim 1 wherein the at least one salt of a transition metal is selected from the group consisting of the halides and sulphides of nickel, cobalt, manganese and chromium.

3. A process as claimed in claim 2 wherein the salt of a transition metal is nickel chloride.

4. A process as claimed in claim 2 wherein the salt of a transition metal is manganese chloride.

5. A process as claimed in claim 2 wherein the salt of a transition metal is cobalt chloride.

6. A process as claimed in claim 1 wherein the cracking catalyst is impregnated with a salt of a transition metal by a solution of the salt in an ionising solvent.

7. A process as claimed in claim 6 wherein the cracking catalyst is impregnated with a salt of a transition metal by a solution of the salt in water.

8. A process as claimed in claim 1 wherein the cracking catalyst is selected from the group consisting of silica/alumina, silica/magnesia, silica/zirconia and silica/boria.

9. A process as claimed in claim 1 wherein the cracking catalyst is silica/alumina containing from about 70-90% by weight of silica.

10. A process as claimed in claim 1 wherein the dimerisation catalyst is activated by heating in a gas selected from the group consisting of molecular oxygen containing gases and inert gases.

11. A process as claimed in claim 10 wherein the gas is air.

12. A process as claimed in claim 10 wherein the gas is nitrogen.

13. A process as claimed in claim 1 wherein the dimeri-

sation reaction is carried out at a temperature in the range 50 to 100° C.

14. A process as claimed in claim 1 wherein the dimerisation reaction is carried out at a pressure in the range 20 to 500 p.s.i.g.

15. A process as claimed in claim 1 wherein the olefine flow rate in the dimerisation reaction is in the range 0.1 to 10 volumes of liquid olefine per volume of catalyst per hour.

16. In a process for the production of detergent alkylate which is biodegradable upon sulphonation, which comprises alkylating an aromatic hydrocarbon in the presence of an alkylation catalyst with an olefin and recovering the detergent alkylate formed, the improvement wherein the olefin is a C₁₀ to C₁₆ olefin having two or more branches produced by dimerizing in the liquid phase straight chain C₅ to C₈ monoolefins in the presence of a catalyst comprising a synthetic petroleum cracking catalyst and at least one salt of a transition metal, the salt being heat stable under catalyst activation and regeneration conditions.

17. In a process for the production of detergent alkylate which is biodegradable upon sulphonation, which comprises alkylating an aromatic hydrocarbon in the presence of an alkylation catalyst with an olefin and recovering the detergent alkylate formed, the improvement wherein the olefin is a C₁₀ to C₁₆ olefin having two or more branches produced by dimerizing in the liquid phase straight chain C₅ to C₈ monoolefins in the presence of a catalyst comprising a synthetic petroleum cracking catalyst and at least one salt of a transition metal selected from the group consisting of nickel, cobalt, manganese and chromium.

18. A process for the production of a C₁₂ olefin having two or more branches from a straight chain hexene feedstock which comprises dimerizing the hexene feedstock in the liquid phase in the presence of a catalyst compris-

ing a synthetic petroleum cracking catalyst and a transition metal salt which is heat stable under catalyst activation and regeneration conditions, and recovering the formed C₁₂ olefin.

19. In a process for the production of detergent alkylate which is biodegradable upon sulphonation, which comprises alkylating an aromatic hydrocarbon in the presence of an alkylation catalyst with an olefin and recovering the detergent alkylate formed, the improvement wherein the olefin is a C₁₂ olefin having two or more branches produced by dimerizing straight chain hexene feedstock in the liquid phase in the presence of a catalyst comprising a synthetic petroleum cracking catalyst and a transition metal salt which is heat stable under catalyst activation and regeneration conditions.

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U.S. CI X.R.

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