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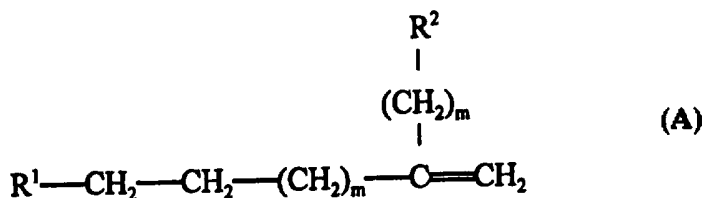
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(54) Title: DIMERIZATION CATALYST AND PROCESS USING ALKYL ALUMINIUM ALKOXIDE

(57) Abstract

A process for producing a vinylidene olefin of the formula (A) where R¹ and R² are the same or different and are hydrogen or alkyl and m is an integer of from 0 to 18, with a catalytically effective amount of a mixture of i) an aluminium compound of the formula R⁴_nAl(OR⁵)_p where R⁴ and R⁵ are the same or different and are alkyl, n is an integer from 0.75 to 2.75, and p is an integer from 0.25 to 2.25, the sum of n and p being 3, at a temperature of from 120 °C to 200 °C whereby a major amount of said vinylidene and deep internal olefin dimer is produced and only a minor amount of a beta internal olefin isomer.



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- 1 -

DIMERIZATION CATALYST AND
PROCESS USING ALKYL ALUMINUM ALKOXIDE

Field of the Invention

This invention relates to a catalyst useful in the dimerization of alpha-olefins. More particularly, this invention relates to an alkyl aluminum alkoxide catalyst to achieve dimerization of alpha-olefins.

Background of the Invention

5 Organoaluminum compounds have been previously utilized in the preparation of catalysts such as Ziegler-type catalysts. These catalysts preparations are based on the ability of organoaluminum compounds to act as reducing agents, i.e., reducing a transition metal to the zero valence state, e.g., U. S. Patent No. 3,113,986.

10 U. S. Patent No. 2,959,607 discloses the preparation of aluminum alkyls which contain at least one n-octyl group by subjecting octene-2 to the action of at least a stoichiometric amount of triisobutyl aluminum in the presence of a cobalt chloride catalyst at substantially atmospheric pressure. The catalyst apparently acts as both an isomerization and displacement catalyst in this process. The aluminum alkyls can be oxidized and hydrolyzed to make octanol-1.

15 U. S. Patent No. 2,962,513 discloses a process for forming longer chain aluminum alkyls by a catalyzed olefin displacement of ethylene from ethyl aluminum compounds using a 100 to 300 percent stoichiometric excess of C₃ or higher alpha-olefins. The process uses salts and oxides of Group VIII metal as catalysts at temperatures of from 50 to 200°C at atmospheric pressure. Ethylene is evolved in the reaction.

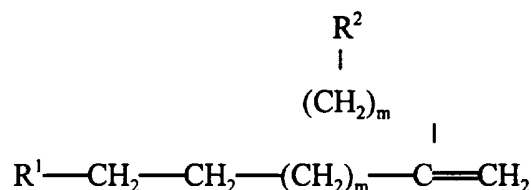
20 U. S. Patent No. 3,784,623 discloses the control of the increased tendency of the alpha-olefins to isomerize to internal olefins, which tendency is associated with catalytic displacement, by adding inhibitors or catalyst inactivators to the process.

25 U. S. Patent No. 4,973,788 discloses a trialkylaluminum catalyst that is useful for dimerizing various vinyl-olefin monomers. The term "vinyl-olefin" is the same as "alpha-olefin" and used interchangeably. This patent notes that the organoaluminum catalyst is used in low concentrations, since high quantities promote the formation of undesirable monomers and dimeric internal olefins.

- 2 -

In accordance with this invention, there is provided a catalyst that is an alkyl aluminum alkoxide of the formula $R^4_nAl(OR^5)_p$, where R^4 and R^5 are alkyl and n is an integer from 0.75 to 2.75, p is an integer from 0.25 to 2.25 and the sum of n and p is 3.

The catalyst is useful in a process for preparing vinylidene olefins of the formula

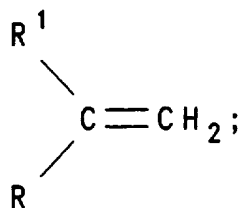


- 5 where R^1 and R^2 are the same or different and are hydrogen or alkyl and m is an integer from 0 to 18.

The vinylidene olefins are useful when oligomerized as oils. Depending on their viscosity, different applications for such oils are known, e.g., as lubricants. These materials are mixtures of different percentages of dimer, trimer, tetramer, pentamer and
 10 higher oligomers which oligomers are produced in different proportions in the oligomerization process. In order to increase the viscosity, processes are used which either produce more of the higher oligomers or some of the lower oligomers are removed such as by distillation. Most low viscosity dimer and trimer products are obtained as by-products of the production of higher viscosity synthetic oils. Due to the increasing use
 15 of dimers in applications such as low temperature lubricants and drilling fluids, methods for their preferential production are of interest.

Detailed Description

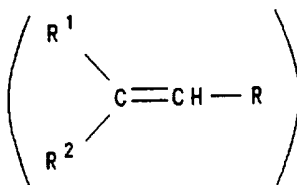
In the specification: olefins are referred to as "vinyl olefins" or $R-CH=CH_2$; "vinylidene olefins" or



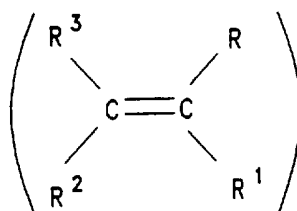
- 3 -

and internal olefins, which are sub-divided as:

"di-substituted olefins" ($R^1-CH=CH-R$) "tri-substituted olefins"



and "tetra-substituted olefins"

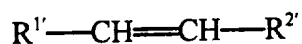


wherein R, R¹, R² and R³ represent a hydrocarbyl group. Internal olefins are also
 5 classified as "beta-internal olefins" in which the double bond is connected to the beta-carbon atom as in:



and "deep internal olefins" which are di-substituted olefins in which the double bond is further towards the center of the olefin as in:

10



wherein R¹ and R² are different by two or four carbon numbers and are aliphatic hydrocarbon groups containing two or more carbon atoms.

The "beta-internal olefins" referred to herein are monomeric. This means they contain the same number of carbon atoms as the initial vinyl-olefins but the olefinic
 15 double bond has moved toward the center of the molecule, by just one carbon number (i.e., the double bond is at the second carbon number).

The "deep internal olefins" referred to herein are dimers of the initial vinyl olefins. For example, a deep internal dimer of 1-octene contains 16 carbon atoms. They differ from vinylidene dimers in that their olefinic double bond is in the linear chain near the center of the molecule.

- 5 The olefins used in making the vinylidene olefin are predominately (at least 50 mole percent) C₄ to C₂₀ straight- or branched-chain monoolefinically unsaturated hydrocarbons (but not less than 5 mole percent) in which the olefinic unsaturation occurs at the 1- or alpha-position of the carbon chain. Typically they have the following formula



- 10 where R² is hydrogen or alkyl, i.e., C₁ to C₁₆ linear or branched alkyl, preferably C₁ to C₆ linear or branched alkyl, most preferably C₁ to C₄ linear or branched alkyl, e.g. methyl or ethyl, and m is an integer from 0 to 16.

- 15 Linear alpha-olefins are commercially available and can be made by the thermal cracking of paraffinic hydrocarbons or by the well-known Ziegler ethylene chain growth and displacement on trialkyl aluminum. Individual olefins may be used as well as mixtures of such olefins. Examples of such olefins are 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-hexadecene and 1-tetra-decene. The more preferred normal alpha-olefin monomers are those containing 8-18 carbon atoms.

- 20 The olefin monomers can also contain minor amounts of from 5 up to 50 and usually less than 25 mole percent of internal olefins and vinylidene olefins. Typically above 70% of said olefin monomers is 8-18 carbon number.

The alpha-olefin of Formula I is contacted with a catalytically effective amount of a catalyst mixture comprising an alkyl aluminum alkoxide.

- 25 The alkyl aluminum alkoxide catalyst has the formula R⁴_nAl(OR⁵)_p where R⁴ and R⁵ are alkyl as defined above, n is an integer from 0.75 to 2.75, p is an integer from 0.25 to 2.25 and sum of n and p is 3. Thus, the alkyl aluminum alkoxide R⁴_{1.5}Al(OR⁵)_{1.5} can be a 1:1 mixture of R⁴Al(OR⁵)₂ and (R⁴)₂AlOR⁵. The compound R⁴Al(OR⁵)₂ can be a minor amount in said mixture, e.g., it can be 5% in R⁴_{1.95}Al(OR⁵)_{1.05}. Preferably, p is 0.5 to 1.8.

- 5 -

The alkyl aluminum alkoxide is readily formed by processes well known to those skilled in the art, i.e., by reaction of a trialkylaluminum with an aliphatic alcohol, e.g., a C₁ to C₂₀ linear or branched aliphatic alcohol such as n-butyl alcohol, n-hexyl alcohol, n-octyl alcohol. Alcohol mixtures may also be used. Alternatively, oxidation of trialkyl aluminum may be carried out by air or oxygen under controlled conditions.

The catalytic mixture, present with the vinyl olefin at the time of dimerization is from about 0.02 to about 0.3 of feed molar ratio of aluminum to vinyl. Catalyst concentrations higher than 0.3 feed molar ratio may be used, if desired, but offer no particular advantage over lesser concentrations. For a typical dimerization reaction as contemplated by the present invention, catalyst concentrations within the range of 0.04 to 0.20 aluminum/vinyl feed molar ratio are preferred.

The dimerization reaction is conducted in a sealed vessel without air at a temperature that is not as low as to retard reaction but not too high such that catalyst activity is diminished due to catalyst decomposition. Thus temperatures in the range of 100°C to 250°C have been found conducive to the dimerization reaction, with a range of 120°C to 200°C being preferred and 120°C to 180°C being most preferred.

The alkyl aluminum alkoxide admixture that is the catalyst of this invention is typically preformed and added to the reaction mixture as such or it may be formed in situ. Thus, for example, a mixture of the alkyl aluminum alkoxide compound, optionally in an inert solvent, may be added to the vinyl olefin to accomplish the present dimerization.

It is also possible to first add the alkyl aluminum alkoxide precursor, i.e., the trialkylaluminum to the olefin reaction mass having the aliphatic alcohol already present. After a period of time suitable to convert the trialkylaluminum into the catalytically active alkyl aluminum alkoxide species (as described herein) the mixture is heated and dimerization effected.

The most preferred embodiment of the invention is a process for dimerizing a mixture of olefins containing 4-20 carbon atoms consisting mainly of vinyl olefins and a minor amount of vinylidene and internal olefins. The process comprises heating the mixture of olefins in contact with an approximate amount of an alkyl aluminum alkoxide of the formula $R^4_nAl(OR^5)_p$, where $n + p = 3$.

- 6 -

EXAMPLES

First, 2499 g or 17.8 g mole of 1-decene (MW=140) is charged into a 3 liter glassware reactor. Next, 218 g or 0.594 g mole of TNOA (Tri Normal Octyl Aluminum, MW=367) is then charged in to the reactor to be mixed with 1-decene. The feed molar ratio of aluminum to vinyl is 0.033 ($0.594 / 17.8 = 0.033$). Then 38.5 g or 0.296 g mole of n-octanol (MW=130) is added to the 1-decene / TNOA mixture slowly while the reaction mixture is stirred. There is a heat release due to oxidation of TNOA. The extent of oxidation of TNOA is 17%. (Note that there are three octyl groups attached to an aluminum molecule, so the extent of oxidation is $0.296 / (0.594 \times 3) = 17\%$.)

10 The reaction mixture is then brought up to the reaction temperature. In this particular example, 170°C. The reaction mixtures during the reaction period are sampled, acid washed, and analyzed by GC and NMR.

15 Table 1 is the composition (Mol% by NMR) of the reaction mixtures at various times. This represents selectivity of 9 wt%, 9 wt% and 82 wt% for beta internal monomer, deep internal dimer and vinylidene dimer, respectively. This compares favorably with example 6 in the U. S. Patent 4,973,788 with selectivity of 15 wt%, 14 wt% and 71 wt% for these three components, respectively. Example 6 in U. S. Patent 4,973,788 was run with aluminum / vinyl feed molar ratio 0.043, at 170°C and without oxidation.

- 7 -

Table 1 Reaction path at 170 °C, aluminum / vinyl feed molar ratio 0.33, 17% oxidized by n-octanol

Time Hr	Mol%			
	Vinyl	Beta Internal	Deep Internal	Vinylidene
0	91.97	2.02	0.30	5.72
0.17	82.3	3.95	0.91	12.8
0.42	67.9	5.14	3.5	23.5
1.42	50.2	8.84	4.57	36.4
1.92	35.6	12.0	5.34	47.2
2.42	33.3	11.4	6.16	49.1
3.42	27.5	12.5	6.46	53.5
3.92	22.6	13.5	6.41	57.5
4.42	20.83	13.74	7.74	57.69
4.92	16.99	13.58	7.79	61.62
5.42	16.42	15.87	5.66	62.05
5.92	12.85	15.28	6.8	65.07

General Procedure

Mixture of TNOA, 1-decene and 1-dodecene is prepared with feed molar ratio of 1/3:1:1 (aluminum/vinyl feed molar ratio = 0.17). Stoichiometric amount of 1-hexanol is added to the mixture for corresponding percent oxidation of aluminum alkyl. The reaction between aluminum alkyl and alcohol to form aluminum alkoxide and paraffin is quantitative. The experiments cover 0%, 11% and 20% oxidation. Reactor temperatures are 120°, 140° and 160°C. The reactor is glassware with nitrogen blanket.

Progress of reaction is analyzed by both GC and NMR. Analytical from GC and NMR are consistent. Mol percent from NMR data are provided. Vinyl is starting alpha olefin monomer. Beta Internal is monomer isomer. Vinylidene and deep internal olefin are dimers. In terms of wt%, vinylidene and deep internal dimer olefins are much greater than those shown by mole%, because vinyl and beta internal olefins are monomer.

- 8 -

EXAMPLE 1

A1: Temperature: 120°C; Oxidation: 0%

Time/Hr.	Mole %			
	Vinyl	Beta Internal	Deep Internal	Vinylidene
0	93.3	2.0	0.5	4.2
0.167	93.2	1.5	1.0	4.3
0.333	92.6	1.9	1.0	4.5
0.5	92.2	1.6	1.2	4.9
0.667	91.6	2.2	1.0	5.2
0.833	91.2	2.5	1.0	5.3
1.0	90.3	2.5	1.2	6.0
1.5	88.8	3.1	1.0	7.1
2.0	86.6	4.2	0.9	8.3
2.5	83.8	4.6	1.8	9.8
3.0	81.8	5.7	1.5	11.0

A2: Temperature: 120°C; Oxidation: 11%

Time/Hr.	Mole %			
	Vinyl	Beta Internal	Deep Internal	Vinylidene
0	93.2	2.2	--	4.6
0.167	92.8	2.2	0.4	4.6
0.333	92.6	2.5	0.1	4.8
0.5	92.4	2.6	0.1	4.9
0.667	91.7	2.9	0.3	5.1
0.833	91.7	2.7	0.3	5.3
1.0	--	--	--	--
1.5	90.1	3.0	0.8	6.1
2.0	88.7	4.0	0.2	7.1
2.5	87.0	4.5	0.2	8.3
3.0	85.9	3.7	1.1	9.2

EXAMPLE 2

B1: Temperature: 140°C; Oxidation: 0%

Time/Hr.	Mole %			
	Vinyl	Beta Internal	Deep Internal	Vinylidene
0	92.7	1.1	1.0	4.7
0.167	91.4	1.5	1.7	5.4
0.333	88.4	2.2	1.5	7.5
0.5	86.4	2.7	1.7	9.2
0.667	83.1	3.5	2.3	11.1
0.833	79.4	4.6	3.2	12.8
1.0	75.9	6.1	2.7	14.4
1.5	67.1	9.0	3.8	20.1
2.0	59.7	11.3	4.2	24.8
2.5	50.8	14.4	5.6	29.2
3.0	42.4	17.4	6.9	33.3

B2: Temperature: 140°C; Oxidation: 11%

Time/Hr.	Mole %			
	Vinyl	Beta Internal	Deep Internal	Vinylidene
0	92.4	2.3	0.2	5.2
0.167	90.4	3.0	0.4	6.2
0.333	89.4	3.3	1.3	6.0
0.5	87.4	4.3	0.6	7.7
0.667	86.2	4.4	0.7	8.6
0.833	84.6	5.7	0.9	8.7
1.0	81.5	6.2	1.4	10.9
1.5	76.8	7.7	1.9	13.7
2.0	71.7	9.3	1.9	17.1
2.5	67.6	12.3	0.9	19.3
3.0	61.0	13.6	2.3	23.1

- 10 -

EXAMPLE 3

C1: Temperature: 160°C; Oxidation: 0%

Time/Hr.	Mole %			
	Vinyl	Beta Internal	Deep Internal	Vinylidene
0	91.6	1.9	1.0	5.5
0.167	85.6	3.1	1.6	9.7
0.333	77.7	5.2	2.3	14.8
0.5	69.8	6.5	3.6	20.1
0.667	63.1	8.2	4.1	24.6
0.833	56.1	10.3	4.8	28.8
1.0	51.1	13.0	4.6	31.3
1.5	37.1	15.1	7.8	40.0
2.0	25.9	19.8	8.1	46.3
2.5	18.7	21.8	9.8	49.8
3.0	14.3	23.0	11.7	51.0

C2: Temperature: 160°C; Oxidation: 11%

Time/Hr.	Mole %			
	Vinyl	Beta Internal	Deep Internal	Vinylidene
0	88.1	4.3	0.9	6.8
0.167	83.7	5.3	1.5	9.5
0.333	78.7	8.1	2.7	11.6
0.5	71.5	9.9	2.7	15.9
0.667	65.7	13.8	2.9	17.5
0.833	59.5	14.1	3.9	22.4
1.0	52.8	16.8	3.9	22.4
1.5	43.5	20.4	5.6	30.5
2.0	33.2	23.9	7.8	35.1
2.5	28.6	27.0	8.3	36.1
3.0	18.9	33.0	9.9	38.2

- 11 -

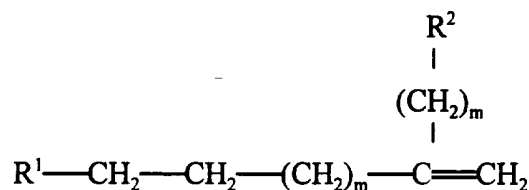
C3: Temperature: 160°C; Oxidation: 20%

Time/Hr.	Mole %			
	Vinyl	Beta Internal	Deep Internal	Vinylidene
0	89.2	3.7	1.9	5.2
0.167	86.1	6.2	1.6	6.1
0.333	80.1	10.3	0.8	8.8
0.5	75.7	13.8	0.9	9.5
0.667	71.0	15.7	1.5	11.8
0.833	66.3	17.8	2.6	13.4
1.0	62.6	19.1	3.3	15.0
1.5	52.5	24.9	4.5	18.1
2.0	43.3	29.2	5.8	21.7
2.5	34.1	34.5	6.5	24.9
3.2	26.2	37.5	8.4	27.9

- 12 -

CLAIMS

1. A process for producing an vinylidene olefin of the formula



- where R^1 and R^2 are the same or different and are hydrogen or alkyl and m is an integer of from 0 to 18, with a catalytically effective amount of a mixture of an aluminum compound of the formula $\text{R}^4_n\text{Al}(\text{OR}^5)_p$ where R^4 and R^5 are the same or different and are alkyl, n is an integer from 0.75 to 2.75, and p is an integer from 0.25 to 2.25, the sum of n and p being 3, at a temperature of from 100°C to 250°C whereby a major amount of said vinylidene olefin and deep internal olefin dimer is produced and only a minor amount of a beta internal isomer olefin.

2. A process of Claim 1 wherein R^1 and R^2 are hydrogen.

3. A process of Claim 1 wherein R^2 is a $\text{C}_2\text{-C}_{16}$ branched aliphatic hydrocarbon group.

4. A process of Claim 1 wherein said temperature is 120°C to 200°C.

5. A process for dimerizing a mixture of alpha olefins containing 4-20 straight or branched chain carbon atoms, said mixture of olefins consisting essentially of 50 to 95 weight percent of vinyl olefins and 5 to 50 weight percent of vinylidene olefins and a minor amount of internal olefins, said process comprising heating said mixture of olefins in contact with a catalytic amount of alkyl aluminum alkoxide with aluminum/vinyl feed molar ratio 0.02 to 0.3 at a temperature of 120°C to 180°C until a substantial amount of said vinyl olefins have dimerized to form dimerized vinylidene and deep internal olefins, said process being characterized in that said vinylidene

- 13 -

olefins which are formed from said alpha olefins are mainly olefins containing 8-36 carbon atoms and have the structure shown in Claim 1.

6. A process of Claim 5 further characterized in that at least 70 weight percent of the alpha olefins in said mixture of olefins is octene, decene, dodecene, tetra decene,
5 hexadecene or octadecene.

7. A dimerization catalyst composition consisting of an alkyl aluminum alkoxide of the formula $R^4_nAl(OR^5)_p$ where R^4 and R^5 are the same or different and are alkyl, n is an integer from 0.75 to 2.75, p is an integer from 0.25 to 2.25 and the sum of n and p is 3.

10 8. The catalyst composition according to Claim 1 wherein said alkyl aluminum oxide is $R^4_nAl(OR^5)_p$, where p is from 0.5 to 1.8 and n is from 1.2 to 2.5.

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/US 95/15246A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C2/30 B01J31/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 973 788 (LIN ET AL) 27 November 1990 cited in the application -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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