COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We, INSTITUT FRANCAIS DU PETROLE

of 4, Avenue de Bois-Preau,
92502 Rueil-Malmaison,
FRANCE

hereby apply for the grant of a standard patent for an invention entitled "IMPROVED PROCESS FOR SYNTHESIZING 1-BUTENE BY DIMERISATION OF ETHYLENE"

which is described in the accompanying provisional complete specification.

Details of basic application(s):

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<tr>
<th>Number of basic application</th>
<th>Name of Convention country in which basic application was filed</th>
<th>Date of basic application</th>
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<tbody>
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<td>83/15 040</td>
<td>FRANCE</td>
<td>20th September, 1983</td>
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<td>20th September, 1983</td>
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DATE OF FILING: 19th September, 1984

To: The Commissioner of Patents.
SYNTHESIZING 1-BUTENE BY DIMERISATION OF ETHYLENE

INSTITUT FRANCAIS DU PETROLE

33288/84 19.9.84
83 15040 20.9.83
83 15041 20.9.83
28.3.85
C07C 2/34  B01J 31/14
C07C 2/32  B01J 31/22

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Claim

1 - An improved process for converting ethylene to 1-butene, wherein ethylene is contacted with a catalyst obtained by reacting an alkyl titanate with an alkylaluminum compound, characterized in that said catalyst results from reacting a premixed mixture of alkyl titanate and ether, in a molar ratio ether/titanate from 0.5 : 1 to 10 : 1, with an aluminum compound of formula AlR$_3$ or AlR$_2$H, wherein each R is a hydrocarbyl radical.
AUSTRALIA

PATENT ACT 1962

COMPLETE SPECIFICATION
(ORIGINAL)
FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:
Lodged:

Complete Specification—Lodged:
Accepted:
Lapsed:
Published:

Priority:

Related Art:


33288/84

TO BE COMPLETED BY APPLICANT

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Complete Specification for the invention entitled: "IMPROVED PROCESS FOR SYNTHESIZING 1-BUTENE
BY DIMERISATION OF ETHYLENE"

The following statement is a full description of this invention, including the best method of performing it known
The object of the present invention is an improved process for dimerizing ethylene to 1-butene.

BACKGROUND OF THE INVENTION

In the U.S. patent 2,943,125, K. ZIEGLER has disclosed a method for dimerizing ethylene to 1-butene by means of a catalyst obtained by admixing a trialkylaluminum compound with a titanium or zirconium tetra-alkoholate; during the reaction, a certain amount of polyethylene of high molecular weight is also formed, which impedes to a large extent the operation. Several improvements have been proposed to reduce the polymer content, particularly in the U.S. patent 3,686,350 which recommends the use of organic phosphorus compounds jointly with the catalyst elements, in the U.S. patent 4,101,600 which claims the treatment of the catalyst with hydrogen or in the U.S. patent 3,879,485 which claims the use of various ethers as solvents for the reaction medium. Although these modifications of the initial catalytic system result in a substantial improvement of the reaction selectivity, they are not of practical use, particularly in an industrial process wherein 1-butene must be separated from the solvent with only traces of polymer compounds.

OBJECT OF THE INVENTION

The object of the present invention is to provide a catalyst having exceptional activity and selectivity. This effect is more substantial than that obtained with the coordinates claimed up to now, such as phosphites or quinines, and is also more substantial than that obtained with ethers when the latter are in an amount corresponding to a use as solvent, or when they are added to the mixture of hydrocarbylaluminum with alkyl titanate. The process has also the advantage of avoiding the use of said ethers as solvents with the corresponding disadvantages (fractionation difficulties). The process also avoids the use of a solvent of external origin since the constituents of the catalyst may be directly admixed within
one of the reaction products or by-products thereof, thus avoiding consumption or recycling of said solvent, which is always difficult to separate from a mixture obtained by oligomerization.

SUMMARY OF THE INVENTION

The invention thus concerns an improved process for converting ethylene to 1-butene, wherein ethylene is contacted with a catalyst obtained by interaction of an alkyl titanate with an alkylaluminum compound, characterized in that said catalyst results from the interaction of a pre-formed mixture of alkyl titanate and ether, in a molar ratio ether/titanate of from 0.5 : 1 to 10 : 1, with an aluminum compound of formula $\text{AlR}_3$ or $\text{AlR}_2\text{H}$, wherein $R$ is a hydrocarbyl radical.

The ethers are thus used in a molar ratio from 0.5 to 10, preferably 1 to 3, more particularly 2 moles of ether per mole of titanium compound. Without relying on any theory, it can be deemed that the ether forms a complex with the titanium atom resulting in the hexacoordination that titanium cannot achieve otherwise than by auto-association. When the ether is used in ratios higher than 10, such as 20 or more, or when it is used as solvent for the reaction, it is observed that the reaction is considerably slowed down and that the selectivity is not so good anymore, in some cases, the reaction does not occur at all.

The aluminum compounds used to prepare the catalyst comply with the general formulas $\text{AlR}_3$ or $\text{AlR}_2\text{H}$ wherein $R$ is a hydrocarbyl radical, preferably an alkyl radical comprising 2 to 6 carbon atoms, for example triethylaluminum, tripropylaluminum, triisobutylaluminum, diisobutylaluminum hydride or trihexylaluminum.

The ethers, as used according to the invention, may be monoethers or polyethers, for example diethyl ether, diisopropyl ether, dibutyl ether, methyl-tert-butylether, tetrahydrofuran, 1,4-dioxane, dihydropyran, ethylene glycol or dimethyl ether.
Exceptional results are obtained with tetrahydrofuran and/or 1,4-dioxane.

The alkyl titanates, as used according to the invention, comply with the general formula Ti (OR)₄, where R is a linear or branched alkyl radical having preferably from 2 to 6 carbon atoms, for example tetraethyl titanate, tetraisopropyl titanate, tetra-n-butyl titanate, tetra-2-ethylhexyl titanate. The catalyst components may be contacted with a hydrocarbon and/or within one or more of the olefinic monomers, such as hexenes, preferably in the presence of ethylene. The molar ratio of the alumina compound to the titanium compound is from about 1 : 1 to 20 : 1 and preferably from about 3 : 1 to 7 : 1.

The titanium concentration in the resultant solution is advantageously from 10⁻⁴ to 0.1 mole per liter and preferably from 2.10⁻³ to 0.1 mole per liter.

The catalyst is usually managed at a temperature from -10 to +80°C, preferably from 0 to +20°C and more preferably from 0 to +40°C. Ethylene, when present in the monomer, is preferably used in an amount corresponding to the conversion of the solution at the prevailing temperature and in the presence of one atmosphere or more.

The resultant catalyst solution may be used in the same way with reaction products. The olefinic substituents can be performed at 20-150°C, preferably 20-80°C and more preferably, 50-70°C. The pressure is preferably from 1 to 8 MPa.

In a particular embodiment of the invention, the catalytic reaction, conducted in batch, a selected volume of the catalyst solution, prepared as mentioned above, is introduced into a reactor provided with usual stirring and cooling systems, and subjected therein to an ethylene pressure, preferably from 0.5 to 8 MPa, at a temperature maintained between 20 and 70°C, preferably between 50 and 70°C. The reactor is fed with ethylene at constant pressure until the total volume of liquid produced amounts to 2 to 50 times the volume of the initially introduced catalytic solution; the catalyst is then destroyed.
by adding water, and the reaction products and the optional solvent are withdrawn and separated.

When proceeding continuously, the operation is preferably as follows: the catalytic solution is introduced with ethylene into a reactor stirred by conventional means or by external recirculation. The temperature is maintained between about 20°C and 70°C, preferably between 50°C and 70°C, and the pressure is preferably from 0.5 to 8 MPa. Through an expansion valve which maintains a constant pressure, a portion of the reaction mixture is discharged at a rate by weight equal to the feeding rate by weight of the supplied fluids. The so-expanded fluid is fed to a distillation column system for separating, on the one hand, 1-hexene from ethylene which is fed back to the reactor and, on the other hand, hexenes and octenes, a portion of which is fed back to the catalyst preparation section. The column bottoms containing the catalyst and heavy products may be burnt, or the recovered catalyst may be recycled.

In a preferred embodiment, the catalyst components are mixed in ethylene atmosphere at a temperature from -10 to +45°C, then the temperature is increased up to 60°C and the dimerization reaction is allowed to continue. In a still more preferred manner, the mixed catalyst components are maintained at a temperature from -10 to +45°C for 30 seconds to 24 hours before increasing the temperature up to 50 - 70°C.

**Example 1**

The following examples illustrate the invention without limitation of the scope thereof.

**Example 1**

A stainless steel autoclave of the Grimard type, of 150 ml capacity, provided with a double jacket, whereby the temperature may be adjusted to 180°C by water circulation, is fed under ethylene atmosphere successively with: 0.5 ml of a tritiated aluminum solution in a cut of hexenes prepared by admixing...
0.25 ml of triethylaluminum with 9.75 ml of hexenes, then with a solution of a tetra-n-butyl titanate-tetrahydrofuran complex prepared by admixing 0.05 ml of tetra-n-butyl titanate with 0.024 ml of tetrahydrofuran and 2.42 ml of hexenes cut. The molar ratio of the tetrahydrofuran to the titanate is 2.1 : 1. After 2 minutes of interaction, the temperature is raised to 55°C and the ethylene pressure to 2 MPa.

After 2h30 of reaction, the ethylene feed is discontinued and the catalyst is destroyed by injecting 2 ml of water under pressure. 1382 g of ethylene as a total were consumed.

In addition to the unreacted ethylene, 0.32 g of n-butane, 92.40 g of 1-butene, 8.16 g of hexenes, 0.17 g of octenes and 0.0027 g of polyethylene are recovered. The analysis of the C4 fraction by gas chromatography with a flame ionization detector shows a mono-1-butene content lower than 10 ppm.

Polyethylene produced is 13,088 g.

In these conditions, the catalyst productivity is increased to 13,088 g of 1-butenes per gram of titanium metal.

EXAMPLE 2 (forming no part of the invention)

In the same apparatus as in example 1, the conditions being unchanged, the amount of 2.1 times increased and the molar ratio of tetrahydrofuran to titanate of 2.1 : 1 instead of 2.1 : 1. After 1 h at 55°C, no ethylene conversion is observed.

EXAMPLE 3 (forming no part of the invention)

In this example, the apparatus and the operating conditions are the same as in example 1 except that the amount of titanium compound in doubled, the amount of aluminum compound is doubled and no tetrahydrofuran is used. 0.05 g of 1-butene, 0.23 g of butane, 11.8 g of hexenes, 0.63 g of octene and 0.1 g of polyethylene are obtained. Resultant 1-butene contains 3.5 ppm of 2-butenes. The catalyst productivity is only 1.02 g of 1-butenes per g of titanium metal.
EXAMPLE 4 (forming no part of the invention)

In successive order, 2.5 ml of a triethylaluminum solution in a cut of hexenes prepared by admixing 0.25 ml of triethylaluminum with 9.75 ml of hexenes, then 0.024 ml of tetrahydrofuran and finally a solution of 0.05 ml of tetra-n-butyl titanate in 2.42 ml of hexenes cut are introduced into the same apparatus as used in example 1, under ethylene atmosphere. The reaction is then conducted under the same conditions and the same procedure as in example 1. The catalyst productivity is only 5,592 g of 1-butene per g of titanium metal. Polyethylene amounts to 70 ppm.

EXAMPLE 5 (forming no part of the invention)

Under ethylene atmosphere, 2.5 ml of a triethylaluminum solution in a cut of hexenes, prepared by admixing 0.25 ml of triethylaluminum with 9.75 ml of hexenes, then a solution of 0.05 ml of tetra-n-butyl titanate in 2.42 ml of hexenes cut, and finally 0.024 ml of tetrahydrofuran are successively introduced in said order into the same apparatus as in example 1. The reaction is performed under the same conditions and with the same procedure as in example 1. The catalyst productivity is only 9,231 g of 1-butene per g of titanium metal. Polyethylene amounts to 42 ppm.

EXAMPLE 6

2.5 ml of a triethylaluminum solution in a cut of hexenes, prepared by admixing 0.25 ml of triethylaluminum with 9.75 ml of hexenes, then a solution of a tetra-n-butyl titanate 1,4-dioxane complex, prepared by admixing 0.05 ml of tetra-n-butyl titanate with 0.024 ml of 1,4-dioxane and 2.42 ml of hexenes cut (the molar ratio of 1,4-dioxane to titanate being 7.07 : 1), are introduced into the same apparatus as in example 1, under ethylene atmosphere, while maintaining the temperature at 18°C. After 2 minutes of interaction, the temperature is brought to 55°C and the ethylene pressure to 3 Mpa.
After 2 h, 0.1 ml of water is added to the reaction mixture. 2 ml of water under pressure, 120 g of ethylene is consumed as a whole.

0.18 g of x-dimene, 0.40 g of 1-butenone, 5.80 g of hexenes.

0.20 g of octenes and 6.52 g of polyethylene are consumed in addition to the reacted ethylene.

The C4 fraction contains 0.60% of x-dimene and a total 2-butenone amount lower than 15 ppm. Polyethylene amounts to 48 ppm.

The catalyst produces 0.1 g of x-dimene per gram of catalyst.

EXAMPLE 3

1.25 ml of a trichloroethane solution of 1.5 ml of water is added to the reaction mixture. 10 ml of hexene is added to the reaction mixture. The mixture is then shaken continuously for 30 min.

2.0 ml of water is then added to the reaction mixture and the mixture is shaken for 30 min.

3.0 ml of water is then added to the reaction mixture and the mixture is shaken for 30 min.

After 3 hours of reaction, the reaction mixture is added to 50 ml of water and the mixture is shaken for 30 min.

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The catalyst produces 0.1 g of x-dimene per gram of catalyst.
Example 5 is repeated except that the glyme amount is increased so as to obtain a molar ratio of glyme to titanate of 330:1 instead of 242:1.
The catalyst productivity is then only 1.35 g of 1-butenone per gram of titanium metal.

EXAMPLE 6
2.5 ml of a triethylaluminum solution in hexene, prepared by adding 1.7 ml of triethylaluminum with 0.2 ml of hexene, then 2.4 ml of a solution of a 9-fold titanate-4-dicarbonyl compound, prepared by adding 0.2 ml of polyglyme titanate with 6.1 ml of 4-dicarbonyl in 14.6 ml of hexene, the molar ratio of polyglyme to titanate being 1:1, are introduced under nitrogen atmosphere into the apparatus as in example 1, while maintaining the temperature at 25°C.
After 5 minutes of interaction, the temperature is raised to 75°C and the nitrogen pressure to 1.5 MPa.
The catalyst is destroyed after 3 hours of reaction.
The catalyst productivity is 0.500 gram of 1-butenone per gram of titanium metal.
THE CLAIMS

1. An apparatus for detecting a predetermined signal from a remote control system, said apparatus comprising:

   a. A receiver
   b. A processor

2. The apparatus of claim 1, wherein:

   a. The processor is further equipped to generate a predetermined signal
   b. The apparatus is further equipped to transmit the predetermined signal

3. A method of detecting a predetermined signal, said method comprising:

   a. Receive the predetermined signal
   b. Process the predetermined signal

4. A processor for detecting a predetermined signal, said processor comprising:

   a. A receiver
   b. A processor
   c. A transmitter

5. The processor of claim 4, wherein:

   a. The processor is further equipped to generate a predetermined signal
   b. The apparatus is further equipped to transmit the predetermined signal

6. A method of detecting a predetermined signal, said method comprising:

   a. Receive the predetermined signal
   b. Process the predetermined signal
   c. Transmit the predetermined signal
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An improved process for converting ethylene to 1-butene, wherein ethylene is contacted with a catalyst obtained by reacting an alkyl aluminum compound with an alkylaluminum compound, characterized in that said catalyst results from reacting a dispersed mixture of alkyl aluminum and other, in molar ratio ethylene to terminal from 6.5:1 to 6:1, with an aluminum component of formula \( \text{Al}_{2} \text{H}_{2} \text{X}_{x} \) or \( \text{Al}_{2} \text{H}_{2} \text{X}_{y} \), admixed with a hydrogen source.

2. A process according to claim 1 wherein the molar ratio of the ethylene to terminal mixture is from about 6:1 to 6:1.

3. A process according to claim 1 wherein the reaction temperature is maintained at a temperature of 100°F to 300°F.

4. A process according to claim 1 wherein the reaction pressure is maintained at a pressure of 150 pounds per square inch to 2000 pounds per square inch.

5. A process according to claim 1 wherein the reaction is conducted at a rate of not more than 1 pound per hour of ethylene.

6. A process according to claim 1 wherein the reaction is conducted at a rate of not more than 1 pound per hour of ethylene at a temperature of 100°F to 300°F.

7. A process according to claim 1 wherein the reaction is conducted at a rate of not more than 1 pound per hour of ethylene at a temperature of 100°F to 300°F.
molar ratio of the aluminum compound to the titanium compound is from 1 : 1 to 20 : 1 and the titanium concentration is from 10^{-4} to 0.5 mole per liter when the catalyst is used for converting ethylene to 1-butene at a temperature from 20 to 150°C under a pressure from 0.5 to 8 MPa.

10 - A process according to claim 9 wherein the temperature is from 20 to 150°C.

Dated this 10th day of September, 1984

INSTITUT FRANCAIS DU PETROLE
By its Patent Attorneys

CLÉMENT HACQ & CO.
Fellows Institute of Patent Attorneys of Australia