

Description**BACKGROUND OF THE INVENTION**

5 This invention relates to alkali metal carbonate supported alkali metal catalysts.

It is known in the art to employ alkali metal carbonate supported elemental alkali metal catalysts for such conversions as propylene dimerization. Several catalyst compositions, as well as methods of preparing these types of catalysts, are known in the art.

10 EP-A-0 409 162, EP-A-0 169 568 and EP-A-0 406 867 relate to dimerization catalysts comprising elemental alkali metal supported on a support. These dimerization catalysts are useful to dimerize olefins. The supports comprise in EP-A-0 409 162 potassium carbonate and an alumina-containing compound, in EP-A-0 169 568 potassium carbonate and, optionally, an inorganic oxide, and in EP-A-0 406 867 alkali metal carbonate, an inorganic nitrate and, optionally, an inorganic oxide and/or a carbonaceous compound. Each catalyst system of the above references can optionally comprise a promoter selected from elemental 15 copper, elemental cobalt and finely divided stainless steel.

The resultant catalyst systems, although useful to dimerize olefins, do not always have a high conversion rate and/or a high isomer ratio of desired product(s) to undesired product(s). Thus, a dimerization process, because of low conversion and/or low isomer ratio, can be more time consuming and require larger, more uneconomical, reactor equipment.

SUMMARY OF THE INVENTION

20 It is an object of this invention to provide an improved catalyst support for a catalyst system useful for the dimerization of olefins.

25 It is an object of this invention to provide an improved catalyst system for the dimerization of olefins.

It is another object of this invention to provide a method to prepare an improved alkali metal carbonate supported elemental alkali metal catalyst system, by the addition of at least one low surface area silica-alumina to the support.

30 It is yet another object of this invention to provide a process to improve catalyst activity and/or the isomer ratio of desired product(s) to undesired product(s) of an alkali metal carbonate supported elemental alkali metal catalyst system.

It is yet another object of this invention to provide an improved process for the dimerization of olefins.

It is yet another object of this invention to provide an improved process to prepare a catalyst support.

35 In accordance with one embodiment of this invention, a process for the preparation of a catalyst support according to claim 6 is provided.

In accordance with another embodiment of this invention, a catalyst composition according to claim 1 is provided. This dimerization catalyst system is useful to dimerize olefins and results in an improved isomer ratio of desired product(s) to undesired product(s) and/or an improved olefin conversion rate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

40 The present invention provides a process to prepare a catalyst support which comprises the steps of preparing a thick paste comprising an alkali metal carbonate, low surface area vitrified silica-alumina, liquid and optionally a carbonaceous compound or finely divided stainless steel; forming a particulate product 45 from said paste; and drying said particulate product. The particulate product can be formed by grinding and sieving prior to calcining, or it can be formed into an extrudate, pellets, tablets, pills, and/or any other granular form prior to calcining. After calcination, the particulate product is contacted with at least one elemental alkali metal to produce a catalyst composition.

Supports

50 As used in this disclosure, the term "support" refers to a carrier for another catalytic component. However, by no means, is the support necessarily an inert material; it is possible that the support can contribute to catalytic activity and selectivity.

55 The catalyst support can be formed by any method known in the art. Thus, commercially available alkali metal carbonate in the form of powder, pellets, granules, or any other form can be treated directly after combining with low surface area vitrified silica-alumina, with at least one elemental alkali metal and, optionally, one or more of the desired promoting materials as discussed more fully below. This form of

support has the advantage of being most readily obtained with a minimum of handling.

The low surface area silica-alumina is vitreous in form. Low surface area silica-aluminas generally include those having a surface area within the range of 0.001 to 50 m²/g. Total pore volume of a suitable low surface area silica-alumina will be within the range of from 0.01 to 1.00 cc/g. Preferably the pore volume will be less than 0.8 cc/g and most preferably, the low surface area silica-alumina will have a pore volume of less than 0.7 cc/gm. Physical characteristics within these ranges can result in a catalyst support that improves percent conversion from reactant(s) to product(s).

Vitreous silica-alumina is a silica-alumina that has been heated until substantially all of the pores of the composition have been fused. The porosity is very low, i.e. usually less than about two percent by volume. The vitrified product is chemically inert due to vitrification, has good durability and high crush strength. It can be used as an inert bed support for catalysts or other materials. Vitreous, or non-porous, silica-aluminas generally include those having a surface area within the range of 0.001 to 1 m²/g. Preferably, the surface area is less than 0.5 m²/g and most preferably, less than 0.1 m²/g. Suitable vitreous silica-aluminas have a pore volume within the range of 0.001 to 1 cc/g. Preferably, the pore volume is less than 0.1 cc/g. Physical properties of vitreous silica-aluminas within these ranges can improve reactant conversion, product selectivity to the desired product(s), and/or the product ratio of desired isomer(s) to undesired isomer(s). One example of vitreous silica-alumina are Denstone products, available from Norton Chemical Process Products, such as for example, Denstone 57. Denstone 57 has a porosity of about 1.5%, surface area of about 0.01 m²/g, and a pore volume of about 0.01 cc/g.

The amount of vitreous, low surface area silica-alumina in the support expressed as weight percent based on the total weight of the final support, comprises from 3 to 15 weight percent, and most preferably the composition comprises from 5 to 12 weight percent vitreous, low surface area silica-alumina based on the weight of the calcined support, to achieve high percent conversion, high selectivity, and a high 4MP1/4MP2 ratio.

Exemplary alkali metal carbonates include carbonates of lithium, sodium, potassium, rubidium, cesium, and mixtures thereof. Potassium carbonate is the most preferred alkali metal carbonate due to ease of use and good compatibility with the preferred elemental alkali metal.

In some circumstances, a large particle size and/or more rugged form of catalyst support is desired, such as, for example, where fixed bed reactions, especially large volume fixed bed reactions, are carried out. One particular technique for support preparation is to form a thick paste comprising an alkali metal carbonate, a low surface area silica-alumina, and a liquid. The liquid can be water or mixtures of water and alcohols or water soluble ketones. In most cases the thick paste can be extruded, pelletized, pillled, or tabletted into desired sizes. The resultant material is then oven dried under conditions of time and temperature such that substantially all liquid is driven off. These types of supports will be referred to as "wet process" alkali metal carbonate supports.

The wet process using alcohol and water as liquid is described in Ewert et al, U.S. 4,810,688. Alcohols suitable for use in preparation of "wet process" catalyst supports are straight chain and branched aliphatic alcohols having from 1 to 7 carbon atoms. The wet process describing water soluble ketone and water is disclosed in Drake U.S. 4,895,819. Water soluble ketones suitable for use in preparation of "wet process" catalyst supports are straight chain and branches water soluble ketones having from 3 to 7 carbon atoms.

In accordance with another technique for the support preparation, an alkali metal carbonate is pelletized with at least one carbonaceous compound. The pelleted support, either as pellets or as smaller crushed particles, is then heated in an oxygen-containing atmosphere under conditions suitable to oxidize in the range of 10 to 90 weight percent of the carbonaceous compound. As a result of this partial oxidation of the pelleted support, the concentration of carbonaceous compound remaining on the surface of the support is substantially less than the concentration of carbonaceous compound remaining on the interior portions of the support. Catalyst support prepared in this manner will be referred to as "carbon containing" alkali metal carbonate support.

The term "carbonaceous compound" is intended to include various forms of the elemental carbon. Examples include, but are not limited to, carbon black, charcoal, coconut charcoal, amorphous graphite, and crystallite graphite.

Once the catalyst support is formed according to any method known in the art, the support must be dried in an oxygen-containing atmosphere at a temperature within the range of 50° to 275°C, preferably from 100° to 275°C, and most preferably from 150° to 275°C for a time of at least 2 hours. The temperature must be high enough to drive off water from the surface as well from the pores. The maximum temperature is determined to be appropriate for the careful oxidation of the carbonaceous compound. Times in excess of about 20 hours generally impart no additional beneficial affect. Thus, times in the range of 2 to 20 hours are useful. Upon completion of calcination, the catalyst support can be stored in a dry

atmosphere. Preferably, the catalyst support is stored under a dry, oxygen-free atmosphere until needed for further treatment.

Catalysts and Promoters

Catalyst systems employed in the practice of this invention comprise one of the catalyst supports described above, at least one elemental alkali metal catalyst, and optionally one or more promoters. It should be recognized, however, that the catalyst systems of the invention can contain additional components which do not adversely affect the catalyst performance, such as, for example, pigments, dyes, processing aids, inert fillers and binders.

The alkali metals contemplated to be within the scope of the invention include lithium, sodium, potassium, rubidium, and cesium. While the proportion of alkali metal combined with the catalyst support can vary appreciably, generally at least about one weight percent of alkali metal based on the total weight of treated support will be employed. Generally, 1 to 20 weight percent alkali metal will be employed with 2 to 15 weight percent preferred. An alkali metal loading of 3 to 10 weight percent based on the total weight of treated support is most preferred for most efficient use of reagents, high catalyst activity and selectivity, high isomer ratio, and ease of catalyst preparation. Potassium is the preferred elemental alkali metal due to its ready availability as well as excellent compatibility with the inventive catalyst support.

The promoters contemplated to be within the scope of the invention include elemental copper, elemental cobalt, finely divided stainless steel, finely divided glass, and mixtures of two or more thereof. The proportion of optional promoter on the alkali metal carbonate support can vary appreciably, but generally, at least one weight percent of the optional promoter based on the total weight of treated support will be employed. The following amounts are provided for additional guidance:

Loading, Weight Percent			
Promoter	Broad	Intermediate	Preferred
Cu	1-30	3-20	5-12
Co	1-50	3-25	5-15
*SS	1-80	3-60	5-50
Glass	1-50	2-25	3-15

*SS = Stainless Steel

The general procedure for preparation of the catalyst systems of the invention, after drying the support, involves heating the catalyst support to a temperature in the range of 80° to 350°C, preferably slightly above the melting point of the particular alkali metal used, and then contacting the catalyst support with at least one elemental alkali metal in a dry, oxygen-free atmosphere, such as, for example N₂ and Ar. The contacting, done in an oxygen-free atmosphere, is preferably carried out with suitable mixing to ensure even distribution. Suitable temperatures for the contacting step will vary with the particular alkali metal employed. For example, with elemental potassium, temperatures in the range of 80° to 100°C are preferred, while with elemental sodium, temperatures in the range of 100° to 140°C are preferred.

While the catalyst support is maintained at or above the melting point of the particular alkali metal used, in an oxygen-free atmosphere, any desired promoter(s), such as, for example, finely divided stainless steel or elemental copper, can be gradually added while the treated catalyst is continually stirred. For example, with potassium, temperatures in the range of 80° to 100°C are employed. The catalyst system is then ready to be charged to the reactor.

Optionally, the catalyst support, once elemental alkali metal and any desired promoters have been deposited thereon, can be subjected to a subsequent heating step, in an oxygen-free atmosphere, to ensure as uniform a distribution as possible of the various promoters on the surface of the alkali metal carbonate support. Thus, the finished catalyst can be subjected to a temperature in the range of 80°C to 350°C for a time in the range of 0.1 to 4 hours. A temperature in the range of 150° to 250°C for a time in the range of 0.5 to 2 hours is presently preferred for the most uniform distribution.

Optionally, prior to charging the reactor, the catalyst system can be mixed with an inert substance to dilute the catalyst system and decrease the rate of olefin dimerization. Any inert substance which has no catalytic activity in an olefin dimerization reaction can be used. One example of such an inert substance is glass beads.

As indicated by the variety of supports, alkali metal components, and promoters included within the scope of the invention, numerous catalyst combinations are possible. Any combination of the alkali metal and optional promoters disclosed can be supported on any alkali metal carbonate support disclosed. Some possible combinations are described in detail in the examples which follow. The combination of support, alkali metal and promoter(s) which one may choose to employ will depend on a variety of variables such as for example, reactor configuration, reaction temperature and pressure, olefin feed employed, rate of olefin feed, and conversions desired.

Reactants

Reactants applicable for use in the process of the invention are olefinic compounds which can (a) self-react, i.e., dimerize, to give useful products such as, for example, the self-reaction of propylene gives 4-methyl-1-pentene; and/or (b) olefinic compounds which can react with other olefinic compounds, i.e., co-dimerize, to give useful products such as, for example, co-dimerization of ethylene plus propylene gives 1-pentene, co-dimerization of ethylene and 1-butene gives 3-methyl-1-pentene and so forth. As used herein, the term "dimerization" is intended to include both self-reaction and "co-dimerization" as defined above.

Suitable dimerizable olefinic compounds are those compounds having from 3 to 30 carbon atoms and having at least one olefinic double bond and at least one allylic hydrogen atom, i.e., at least one hydrogen atom attached to a carbon atom adjacent to a double-bonded carbon atom. Exemplary compounds include, but are not limited to, acyclic and cyclic olefins such as, for example, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, 1-hexene, 2-hexene, 3-hexene, 1-heptene, 2-heptene, 3-heptene, the four normal octenes and the four normal nonenes; 3-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-pentene, 3-methyl-2-pentene, 4-methyl-1-pentene, 4-methyl-2-pentene and tetramethylethylene; cyclopentene, cyclohexene, methylcyclopentene, methylcyclohexene, and mixtures of any two or more thereof.

Suitable co-dimerizable olefinic compounds are those compounds having from 2 to 30 carbon atoms, including all the compounds contemplated within the scope of "dimerizable" olefinic compounds as indicated above. In addition, olefinic compounds which do not have at least one allylic hydrogen atom are also included within the scope of co-dimerizable olefins. Exemplary compounds in addition to those indicated above, include, but are not limited to ethylene, 3,3-dimethyl-1-butene, ditertiarybutyl ethylene and mixtures of any two or more thereof.

The compounds indicated above as dimerizable olefinic compounds are capable of undergoing both self-reaction, i.e., dimerization, and cross-reaction, i.e., co-dimerization, with other members of the same group or with those compounds designated as co-dimerizable. The co-dimerizable compounds which do not have at least one allylic hydrogen may be capable of isomerization to form an olefin having an allylic hydrogen under the reaction conditions employed. If such isomerization is not possible, then those non-isomerizable, co-dimerizable compounds which do not have at least one allylic hydrogen must be contacted with at least one of the "dimerizable" compounds in order to facilitate the desired co-dimerization reaction. In other words, the co-dimerizable compounds which do not have at least one allylic hydrogen atom and are not capable of isomerization to produce an olefin having at least one allylic hydrogen are therefore not capable of reacting with themselves under the reaction conditions employed for the dimerization reaction.

Reaction Conditions

The dimerization reaction of the invention can be carried out using either batch or continuous types of operation, although the catalysts of the invention are particularly well suited for continuous, fixed bed, operation. Suitable equipment, such as, for example, autoclaves and tubular reactors, as are well known in the art can be employed. No special materials of construction are required so that steel, stainless steel, or glass-lined reactors, can be employed.

The reaction temperature can vary depending on the catalyst and feed(s) employed. Typically, a temperature range of 50° to 250°C is suitable. Temperatures of 80° to 200°C are preferred with a range of 120° to 170°C most preferred because optimum reaction rates are obtained with minimum by-product formation.

The dimerization reaction can be carried out by contacting the dimerizable olefins with catalyst in the liquid phase or the gas phase, depending on the structure and molecular weight of the olefin, as well as reaction temperature and pressure employed. Pressure during the dimerization reaction can vary between wide limits. In general, higher pressures favor the progress of the reaction. Thus, pressures of atmospheric up to 69 MPa (10,000 psig) and higher are suitable. Preferably, pressures of 0.79 to 34.6 MPa (100 to 5,000 psig) are employed, with pressures of 7.0 to 27.7 MPa (1,000 to 4,000 psig) most preferred in order to

achieve a good balance between reaction rate and minimize equipment and operating costs necessitated by very high reaction pressures.

If the reaction is carried out in the liquid phase, solvents or diluents for the reactants can be used. Saturated aliphatic hydrocarbons, e.g., pentane, hexane, cyclohexane, dodecane; aromatic compounds, preferably those without an alpha-hydrogen (which would be capable of undergoing alkylation under the reaction conditions) such as benzene and chlorobenzene are suitable. If the reaction is carried out in the gaseous phase, diluents such as aliphatic hydrocarbons, for example methane, ethane and/or substantially inert gases, e.g., nitrogen, argon, can be present.

The contact time required for the dimerization reaction depends upon several factors, such as, for example, the activity of the catalyst, temperature, pressure, structure of the reactants employed and level of conversion desired. The length of time during which the dimerizable olefinic compounds are contacted with catalyst can vary conveniently between 0.1 seconds and 24 hours although shorter and longer contact times can be employed. Preferably, times of one minute to 5 hours are employed. Where reaction is carried out in continuous fashion, it is convenient to express the reactant/catalyst contact time in terms of weight hourly space velocity (WHSV), i.e., the ratio of the weight of reactant which comes in contact with a given weight of catalyst per unit time. Thus, a WHSV of 0.1 to 10 will be employed. A WHSV of 0.5 to 5 is preferred, with 1 to 4 WHSV most preferred for optimum catalyst productivity.

Products

The olefinic products of the invention have established utility in a wide variety of applications, such as, for example, as monomers for use in the preparation of homopolymers, copolymers, terpolymers, e.g., as the third component of ethylene-propylene terpolymers useful as synthetic elastomers.

A further understanding of the present invention and its advantages will be provided by reference to the following example.

EXAMPLES

In each of the following examples, typically, the dimerization of propylene was carried out in a steam heated 316 stainless steel tubular reactor (1.27 cm X 50.8 cm) ((1/2" X 20")). The catalyst system (27 grams; density about 0.84 g/mL), bounded above and below by small volumes of glass beads, was combined with 25 grams of an inert substance, i.e., no dimerization catalytic activity, to dilute the catalyst system and thus reduce and control the reaction rate. The contents of the tubular reactor were heated to the reaction temperature of about 160°C at about 10.5 MPa (1500 psig) and propylene was pumped into the reactor at a rate of about 120 mL/hr. After about 1.5 hours of reaction time and each one hour thereafter for the following 6 hours, a sample was collected and analyzed by gas liquid chromatograph (GLC). The summarized results represent the analysis of the last dimerization sample collected.

The catalyst support was prepared from varying amounts of commercially available anhydrous potassium carbonate (JT Baker, ACS reagent grade), a low surface area silica-alumina, and deionized water. Sufficient water was added to the solid particles to form a thick paste. Usually, about 2 milliliters of water were added to about 1 gram of solid material. The thick paste was thoroughly mixed and then dried at about 85°C in a vacuum oven for at least two hours in the presence of air. The dried paste was ground to about 3.35 mm (six mesh) and dried at about 250°C for about 3 hours in an oxygen-containing atmosphere.

The resultant support was allowed to cool and maintained at a temperature of about 85°C, in an oxygen-free atmosphere, at which time about 5 weight percent of elemental potassium based on weight of final calcined support was added. The catalyst support and catalyst system were kept under a dry, inert atmosphere during and after preparation.

Catalysts and the results of the corresponding propylene dimerizations are summarized in the Table. Percent propylene conversion, as used in the Table, is the weight percent of reactant propylene that was converted to any type of reaction product. Percent selectivity, is the weight percent of product that was 4-methyl-1-pentene (4MP1). The isomer ratio, 4-methyl-1-pentene/4-methyl-2-pentene (4MP1/4MP2), is the mass ratio of 4MP1 to 4MP2 in the final product. The isomer ratio data is significant because 4MP1, the desired product, and 4MP2, the undesired product, are difficult to separate.

Example

The low surface silica-alumina used in the Example is vitrified, non-porous type and is commercially available as Denstone 57, supplied by Norton Chemical Process Products. Denstone 57 has a surface area

of 0.011 to 0.016 m²/gm, free space of 40%, particle density 2.4 gm/cc, Mohs' hardness 6.5, modulus of rupture ASTM C-133 of 55.2 MPa (8,000 psi), linear expansion coefficient 9.5×10^{-6} m/m °C, and specific heat at 100 °C of 1.05 J/g (0.25 cal/gm). The chemical composition in weight percent is 38% Al₂O₃; 56% SiO₂; 1.9% Fe₂O₃ + TiO₂; 1.7% MgO and CaO; and 1.9% Na₂O and K₂O.

- 5 In all Runs, the catalyst used was about 5 weight percent elemental potassium based on the weight of the final calcined support.

Table

Run No.	Support	Catalyst	Conversion, %	Selectivity, %	4MP1/4MP2
201	K ₂ CO ₃ + 10% Denstone 57*	5% K	24.1	88.0	20
202 (control run)	K ₂ CO ₃ + 20% Denstone 57*	5% K	18.8	86.8	17
203 (control run)	K ₂ CO ₃ no Denstone 57	5% K	21.9	88.0	19

15 * % by weight, based on weight of potassium carbonate used

The data in the Table show that the best overall propylene dimerization catalyst is that in Run 201, based on high levels of percent conversion, selectivity, and isomer ratio, although other formulations are effective propylene dimerization catalysts.

Claims

Claims for the following Contracting States : AT, BE, DE, DK, FR, GB, IT, NL, SE

- 25 1. A catalyst composition comprising:
 - (a) at least one elemental alkali metal; and
 - (b) a support consisting of alkali metal carbonate, at least one low surface area vitrified silica-alumina compound, and, optionally, at least one carbonaceous compound, one or more promoters, pigments dyes, processing aids, inert fillers or binders,
- 30 wherein said support has been dried at a temperature of 50 to 275 °C, wherein component (a) is supported on component (b), wherein said vitrified silica alumina has a surface area in the range of 0.001 to 1 m²/g and a pore volume in the range of 0.001 to 1 ml/g, and is present in an amount of 3 to 15 weight percent based on total weight of the support.
- 35 2. The composition of claim 1 wherein said elemental alkali metal is potassium.
3. The composition of claim 1 or 2 wherein said elemental alkali metal is present in an amount from 1 to 20 weight percent based on the total weight of said support.
- 40 4. The composition of any of the preceding claims wherein said alkali metal carbonate is potassium carbonate.
- 45 5. The catalyst composition of any of claims 2 to 4, wherein said potassium carbonate is present in an amount of 85 to 97 weight percent.
- 50 6. A process for the preparation of a catalyst support as defined in any of the claims 1, 4 or 5, comprising
 - (a) preparing a thick paste comprising alkali metal carbonate, a low surface area vitrified silica-alumina, and a liquid;
 - (b) forming a particulate product from said paste; and
 - (c) drying said particulate product.
- 55 7. A process for producing a catalyst composition which comprises contacting a support as defined in any of the claims 1, 4 or 5 with at least one elemental alkali metal.
8. The process of claim 7 wherein said contacting is effected under an oxygen-free atmosphere and at a temperature causing the elemental alkali metal to melt.



of 0.011 to 0.016 m²/gm, free space of 40%, particle density 2.4 gm/cc, Mohs' hardness 6.5, modulus of rupture ASTM C-133 of 55.2 MPa (8,000 psi), linear expansion coefficient 9.5×10^{-6} m/m °C, and specific heat at 100 °C of 1.05 J/g (0.25 cal/gm). The chemical composition in weight percent is 38% Al₂O₃; 56% SiO₂; 1.9% Fe₂O₃ + TiO₂; 1.7% MgO and CaO; and 1.9% Na₂O and K₂O.

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* % by weight, based on weight of potassium carbonate used

The data in the Table show that the best overall propylene dimerization catalyst is that in Run 201, based on high levels of percent conversion, selectivity, and isomer ratio, although other formulations are effective propylene dimerization catalysts.

Claims

Claims for the following Contracting States : AT, BE, DE, DK, FR, GB, IT, NL, SE

1. A catalyst composition comprising:

- (a) at least one elemental alkali metal; and
- (b) a support consisting of alkali metal carbonate, at least one low surface area vitrified silica-alumina compound, and, optionally, at least one carbonaceous compound, one or more promoters, pigments dyes, processing aids, inert fillers or binders,

wherein said support has been dried at a temperature of 50 to 275 °C,

wherein component (a) is supported on component (b),

wherein said vitrified silica alumina has a surface area in the range of 0.001 to 1 m²/g and a pore volume in the range of 0.001 to 1 ml/g, and is present in an amount of 3 to 15 weight percent based on total weight of the support.

2. The composition of claim 1 wherein said elemental alkali metal is potassium.

3. The composition of claim 1 or 2 wherein said elemental alkali metal is present in an amount from 1 to 20 weight percent based on the total weight of said support.

4. The composition of any of the preceding claims wherein said alkali metal carbonate is potassium carbonate.

5. The catalyst composition of any of claims 2 to 4, wherein said potassium carbonate is present in an amount of 85 to 97 weight percent.

6. A process for the preparation of a catalyst support as defined in any of the claims 1, 4 or 5, comprising

- (a) preparing a thick paste comprising alkali metal carbonate, a low surface area vitrified silica-alumina, and a liquid;

(b) forming a particulate product from said paste; and

(c) drying said particulate product.

7. A process for producing a catalyst composition which comprises contacting a support as defined in any of the claims 1, 4 or 5 with at least one elemental alkali metal.

8. The process of claim 7 wherein said contacting is effected under an oxygen-free atmosphere and at a temperature causing the elemental alkali metal to melt.



9. The process of claim 7 or 8 wherein said elemental alkali metal is as defined in claim 2 or 3.
10. The process of any of the claims 7 to 9 further comprising contacting said catalyst system with at least one promoter selected from finely divided stainless steel, elemental copper, elemental cobalt, finely divided glass, and mixtures thereof.
11. The process of claim 6 wherein said alkali metal carbonate is defined as in claim 4.
12. The process of claim 6 or 11 wherein said particulate product is formed by
 - (a) drying said thick paste to remove substantially all liquid from said paste to form a dried product;
 - (b) crushing the dried product of step (a); and
 - (c) collecting a substantially uniform particle size particulate product.
13. The use of the catalyst composition as defined in any of the claims 1 to 5 and 7 to 9 for the dimerization of olefins.
14. The use of claim 13 wherein said dimerization comprises a temperature within the range of 80 to 200 °C, a pressure within the range of 6.9 to 27.6 MPa, and a weight hourly space velocity within the range of 0.1 to 10, using olefinic compounds having from 3 to 30 carbon atoms.

Claims for the following Contracting State : ES

1. A process for preparing a catalyst composition comprising:
 - (a) at least one elemental alkali metal; and
 - (b) a support consisting of alkali metal carbonate, at least one low surface area vitrified silica-alumina compound, and, optionally, at least one carbonaceous compound, one or more promoters, pigments, dyes, processing aids, inert fillers or binders,
 wherein said support has been dried at a temperature of 50 to 275 °C,
 wherein component (a) is supported on component (b),
 wherein said vitrified silica alumina has a surface area in the range of 0.001 to 1 m²/g and a pore volume in the range of 0.001 to 1 ml/g, and is present in an amount of 3 to 15 weight percent based on total weight of the support,
 wherein the process for preparing the catalyst composition comprises contacting the support produced by
 - (a) preparing a thick paste comprising alkali metal carbonate, a low surface area vitrified silica-alumina, and a liquid;
 - (b) forming a particulate product from said paste; and
 - (c) drying said particulate product,
 with the at least one elemental alkali metal.
2. The process of claim 1 wherein said elemental alkali metal is potassium.
3. The process of claim 1 or 2 wherein said elemental alkali metal is present in an amount from 1 to 20 weight percent, based on the total weight of said support.
4. The process of any of the preceding claims wherein said alkali metal carbonate is potassium carbonate.
5. The process of any of claims 2 to 4, wherein said potassium carbonate is present in an amount of 85 to 97 weight percent.
6. A process for the preparation of a catalyst support as defined in any of the claims 1, 4 or 5, comprising
 - (a) preparing a thick paste comprising alkali metal carbonate, a low surface area vitrified silica-alumina, and a liquid;
 - (b) forming a particulate product from said paste; and
 - (c) drying said particulate product.
7. A process for producing a catalyst composition which comprises contacting a support as defined in any of the claims 1, 4 or 5 with at least one elemental alkali metal.



8. The process of claim 7 wherein said contacting is effected under an oxygen-free atmosphere and at a temperature causing the elemental alkali metal to melt.
9. The process of claim 7 or 8 wherein said elemental alkali metal is as defined in claim 2 or 3.
10. The process of any of the claims 7 to 9 further comprising contacting said catalyst system with at least one promoter selected from finely divided stainless steel, elemental copper elemental cobalt, finely divided glass, and mixtures thereof.
11. The process of claim 6 wherein said alkali metal carbonate is defined as in claim 4.
12. The process of claim 6 or 11 wherein said particulate product is formed by
 - (a) drying said thick paste to remove substantially all liquid from said paste to form a dried product;
 - (b) crushing the dried product of step (a); and
 - (c) collecting a substantially uniform particle size particulate product.
13. The use of the catalyst composition as defined in any of the claims 1 to 5 and 7 to 9 for the dimerization of olefins.
14. The use of claim 13 wherein said dimerization comprises a temperature within the range of 80 to 200 °C, a pressure within the range of 6.9 to 27.6 MPa, and a weight hourly space velocity within the range of 0.1 to 10, using olefinic compounds having from 3 to 30 carbon atoms.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

1. Katalysatorzusammensetzung, umfassend:
 - (a) mindestens ein elementares Alkalimetall; und
 - (b) einen Träger, der aus Alkalimetallcarbonat, mindestens einer verglasten Siliciumdioxid-Aluminiumoxid-Verbindung mit geringer Oberfläche und gegebenenfalls mindestens einer kohlenstoffartigen Verbindung, einem oder mehreren Promotoren, Pigmenten, Farbstoffen, Verarbeitungshilfsmitteln, inerten Füllstoffen oder Bindemitteln besteht,

wobei der Träger bei einer Temperatur von 50 bis 275 °C getrocknet worden ist,

wobei die Komponente (a) auf die Komponente (b) als Träger aufgebracht ist,

wobei das verglaste Siliciumdioxid-Aluminiumoxid eine Oberfläche im Bereich von 0,001 bis 1 m²/g und ein Porenvolumen im Bereich von 0,001 bis 1 ml/g aufweist und in einer Menge von 3-15 Gew.-%, bezogen auf das Gesamtgewicht des Trägers, vorliegt.
2. Zusammensetzung nach Anspruch 1, wobei es sich beim elementaren Alkalimetall um Kalium handelt.
3. Zusammensetzung nach Anspruch 1 oder 2, wobei das elementare Alkalimetall in einer Menge von 1 bis 20 Gew.-%, bezogen auf das Gesamtgewicht des Trägers vorhanden ist.
4. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei es sich beim Alkalimetallcarbonat um Kaliumcarbonat handelt.
5. Katalysatorzusammensetzung nach einem der Ansprüche 2 bis 4, wobei das Kaliumcarbonat in einer Menge von 85 bis 97 Gew.-% vorliegt.
6. Verfahren zur Herstellung eines Katalysatorträgers gemäß der Definition in einem der Ansprüche 1, 4 oder 5, umfassend:
 - (a) die Herstellung einer dickflüssigen Paste mit einem Gehalt an Alkalimetallcarbonat, einem verglasten Siliciumdioxid-Aluminiumoxid von geringer Oberfläche und einer Flüssigkeit;
 - (b) die Bildung eines teilchenförmigen Produkts aus dieser Paste; und
 - (c) die Trocknung des teilchenförmigen Produkts.
7. Verfahren zur Herstellung einer Katalysatorzusammensetzung, umfassend das Kontaktieren eines Trägers nach einem der Ansprüche 1, 4 oder 5 mit mindestens einem elementaren Alkalimetall.



8. Verfahren nach Anspruch 7, wobei das Kontaktieren unter einer sauerstofffreien Atmosphäre und bei einer Temperatur, die ein Schmelzen des elementaren Alkalimetalls bewirkt, durchgeführt wird.
9. Verfahren nach Anspruch 7 oder 8, wobei das elementare Alkalimetall der Definition in Anspruch 2 oder 3 entspricht.
10. Verfahren nach einem der Ansprüche 7 bis 9, ferner umfassend das Kontaktieren des Katalysatorsystems mit mindestens einem Promotor, der unter feinverteiltem rostfreiem Stahl, elementarem Kupfer, elementarem Cobalt, feinverteiltem Glas und Gemischen davon ausgewählt ist.
11. Verfahren nach Anspruch 6, wobei das Alkalimetallcarbonat der Definition in Anspruch 4 entspricht.
12. Verfahren nach Anspruch 6 oder 11, wobei das teilchenförmige Produkt gebildet wird durch
 - (a) Trocknen der dickflüssigen Paste unter Entfernung der im wesentlichen gesamten Flüssigkeit aus der Paste zur Bildung eines getrockneten Produkts;
 - (b) Zerkleinern des getrockneten Produkts von Stufe (a); und
 - (c) Gewinnen eines teilchenförmigen Produkts mit im wesentlichen gleichmäßiger Teilchengröße.
13. Verwendung der Katalysatorzusammensetzung gemäß der Definition in einem der Ansprüche 1 bis 5 und 7 bis 9 für die Dimerisation von Olefinen.
14. Verwendung nach Anspruch 13, wobei die Dimerisation eine Temperatur im Bereich von 80 bis 200 °C, einen Druck im Bereich von 6,9 bis 27,6 MPa und eine auf das Gewicht bezogene Raumgeschwindigkeit im Bereich von 0,1 bis 10 umfaßt, wobei olefinische Verbindungen mit 3 bis 30 Kohlenstoffatomen verwendet werden.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung einer Katalysatorzusammensetzung, umfassend:
 - (a) mindestens ein elementares Alkalimetall; und
 - (b) einen Träger, der aus Alkalimetallcarbonat, mindestens einer verglasten Siliciumdioxid-Aluminiumoxid-Verbindung mit geringer Oberfläche und gegebenenfalls mindestens einer kohlenstoffartigen Verbindung, einem oder mehreren Promotoren, Pigmenten, Farbstoffen, Verarbeitungshilfsmitteln, inerten Füllstoffen oder Bindemitteln besteht,
 wobei der Träger auf eine Temperatur von 50 bis 275 °C getrocknet worden ist,
 wobei die Komponente (a) auf die Komponente (b) als Träger aufgebracht ist,
 wobei das verglaste Siliciumdioxid-Aluminiumoxid eine Oberfläche im Bereich von 0,001 bis 1 m²/g und ein Porenvolumen im Bereich von 0,001 bis 1 ml/g aufweist und in einer Menge von 3-15 Gew.-%, bezogen auf das Gesamtgewicht des Trägers vorliegt,
 wobei das Verfahren zur Herstellung der Katalysatorzusammensetzung das Kontaktieren des durch
 - (a) Herstellung einer dickflüssigen Paste mit einem Gehalt an Alkalimetallcarbonat, einem verglasten Siliciumdioxid-Aluminiumoxid von geringer Oberfläche und einer Flüssigkeit;
 - (b) Bildung eines teilchenförmigen Produkts aus dieser Paste; und
 - (c) Trocknung des teilchenförmigen Produkts
 hergestellten Trägers mit mindestens einem elementaren Alkalimetall umfaßt.
2. Verfahren nach Anspruch 1, wobei es sich beim elementaren Alkalimetall um Kalium handelt.
3. Verfahren nach Anspruch 1 oder 2, wobei das elementare Alkalimetall in einer Menge von 1 bis 20 Gew.-%, bezogen auf das Gesamtgewicht des Trägers vorhanden ist.
4. Verfahren nach einem der vorstehenden Ansprüche, wobei es sich beim Alkalimetallcarbonat um Kaliumcarbonat handelt.
5. Verfahren nach einem der Ansprüche 2 bis 4, wobei das Kaliumcarbonat in einer Menge von 85 bis 97 Gew.-% vorliegt.



6. Verfahren zur Herstellung eines Katalysatorträgers gemäß der Definition in einem der Ansprüche 1, 4 oder 5, umfassend:
 - (a) die Herstellung einer dickflüssigen Paste mit einem Gehalt an Alkalimetallcarbonat, einem verglasten Siliciumdioxid-Aluminiumoxid von geringer Oberfläche und einer Flüssigkeit;
 - (b) die Bildung eines teilchenförmigen Produkts aus dieser Paste; und
 - (c) die Trocknung des teilchenförmigen Produkts.
7. Verfahren zur Herstellung einer Katalysatorzusammensetzung, umfassend das Kontaktieren eines Trägers nach einem der Ansprüche 1, 4 oder 5 mit mindestens einem elementaren Alkalimetall.
8. Verfahren nach Anspruch 7, wobei das Kontaktieren unter einer sauerstofffreien Atmosphäre und bei einer Temperatur, die ein Schmelzen des elementaren Alkalimetalls bewirkt, durchgeführt wird.
9. Verfahren nach Anspruch 7 oder 8, wobei das elementare Alkalimetall der Definition in Anspruch 2 oder 3 entspricht.
10. Verfahren nach einem der Ansprüche 7 bis 9, ferner umfassend das Kontaktieren des Katalysatorsystems mit mindestens einem Promotor, der unter feinverteiltem rostfreiem Stahl, elementarem Kupfer, elementarem Cobalt, feinverteiltem Glas und Gemischen davon ausgewählt ist.
11. Verfahren nach Anspruch 6, wobei das Alkalimetallcarbonat der Definition in Anspruch 4 entspricht.
12. Verfahren nach Anspruch 6 oder 11, wobei das teilchenförmige Produkt gebildet wird durch
 - (a) Trocknen der dickflüssigen Paste unter Entfernung der im wesentlichen gesamten Flüssigkeit aus der Paste zur Bildung eines getrockneten Produkts;
 - (b) Zerkleinern des getrockneten Produkts von Stufe (a); und
 - (c) Gewinnen eines teilchenförmigen Produkts mit im wesentlichen gleichmäßiger Teilchengröße.
13. Verwendung der Katalysatorzusammensetzung gemäß der Definition in einem der Ansprüche 1 bis 5 und 7 bis 9 für die Dimerisation von Olefinen.
14. Verwendung nach Anspruch 13, wobei die Dimerisation eine Temperatur im Bereich von 80 bis 200 °C, einen Druck im Bereich von 6,9 bis 27,6 MPa und eine auf das Gewicht bezogene Raumgeschwindigkeit im Bereich von 0,1 bis 10 umfaßt, wobei olefinische Verbindungen mit 3 bis 30 Kohlenstoffatomen verwendet werden.

Revendications

Revendications pour les Etats contractants suivants : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

1. Une composition de catalyseur comprenant :
 - (a) au moins un métal alcalin élémentaire ; et
 - (b) un support consistant en un carbonate de métal alcalin, au moins un composé de silice-alumine vitrifiée à faible surface spécifique et, éventuellement, au moins un composé carboné, un ou plusieurs promoteurs, pigments, colorants, aides de traitement, agents de remplissage inertes ou liants,
 où le support a été séché à une température de 50 à 275 °C,
 où le composant (a) est supporté sur le composant (b),
 où la silice-alumine vitrifiée a une surface spécifique dans la plage allant de 0,001 à 1 m²/g et un volume de pores dans la plage allant de 0,001 à 1 ml/g, et est présente en une quantité de 3 à 15 % en poids par rapport au poids total du support.
2. La composition de la revendication 1, où le métal alcalin élémentaire est le potassium.
3. La composition de la revendication 1 ou 2, où le métal alcalin élémentaire est présent en une quantité de 1 à 20 % en poids par rapport au poids total du support.



4. La composition de l'une des revendications précédentes, où le carbonate de métal alcalin est le carbonate de potassium.
5. La composition de catalyseur de l'une des revendications 2 à 4, où le carbonate de potassium est présent en une quantité de 85 à 97 % en poids.
6. Un processus pour la préparation d'un support de catalyseur tel que défini dans l'une des revendications 1, 4 ou 5, comprenant :
 - (a) la préparation d'une pâte épaisse comprenant du carbonate de métal alcalin, une silice-alumine vitrifiée à faible surface spécifique et un liquide;
 - (b) la formation d'un produit particulaire à partir de cette pâte ; et
 - (c) le séchage de ce produit particulaire.
7. Un processus pour produire une composition de catalyseur, qui comprend la mise en contact d'un support tel que défini dans l'une des revendications 1, 4 ou 5 avec au moins un métal alcalin élémentaire.
8. Le processus de la revendication 7, où la mise en contact est opérée dans une atmosphère dépourvue d'oxygène et à une température provoquant la fusion du métal alcalin élémentaire.
9. Le processus de la revendication 7 ou 8, où le métal alcalin élémentaire est tel que défini dans la revendication 2 ou 3.
10. Le processus de l'une des revendications 7 à 9, comprenant en outre la mise en contact du système catalyseur avec au moins un promoteur choisi parmi l'acier inoxydable finement divisé, le cuivre élémentaire, le cobalt élémentaire, le verre finement divisé et leurs mélanges.
11. Le processus de la revendication 6, où le carbonate de métal alcalin est tel que défini dans la revendication 4.
12. Le processus de la revendication 6 ou 11, où le produit particulaire est formé par :
 - (a) séchage de la pâte épaisse de manière à éliminer de cette pâte pratiquement la totalité du liquide de manière à former un produit séché ;
 - (b) broyage du produit séché de l'étape (a) ; et
 - (c) recueil d'un produit particulaire de dimensions de particule essentiellement uniforme.
13. L'utilisation de la composition de catalyseur telle que définie dans l'une des revendications 1 à 5 et 7 à 9 pour la dimérisation des oléfines.
14. L'utilisation de la revendication 13, où la dimérisation comprend une température dans la plage allant de 80 à 200 °C, une pression dans la plage allant de 6,9 à 27,6 MPa et une vitesse spatiale horaire pondérale dans la plage allant de 0,1 à 10, en utilisant des composés oléfiniques ayant de 3 à 30 atomes de carbone.

Revendications pour l'Etat contractant suivant : ES

1. Un processus de préparation d'une composition de catalyseur comprenant :
 - (a) au moins un métal alcalin élémentaire ; et
 - (b) un support consistant en un carbonate de métal alcalin, au moins un composé de silice-alumine vitrifiée à faible surface spécifique et, éventuellement, au moins un composé carboné, un ou plusieurs promoteurs, pigments, colorants, aides de traitement, agents de remplissage inertes ou liants,
 où le support a été séché à une température de 50 à 275 °C,
 où le composant (a) est supporté sur le composant (b),
 où la silice-alumine vitrifiée a une surface spécifique dans la plage allant de 0,001 à 1 m²/g et un volume de pores dans la plage allant de 0,001 à 1 ml/g, et est présente en une quantité de 3 à 15 % en poids par rapport au poids total du support
 où le processus de préparation de la composition de catalyseur comprend la mise en contact du



support produit par

- (a) préparation d'une pâte épaisse comprenant du carbonate de métal alcalin, une silice-alumine vitrifiée à faible surface spécifique et un liquide;
 - (b) formation d'un produit particulaire à partir de cette pâte ; et
 - (c) séchage de ce produit particulaire,
- avec ledit métal alcalin élémentaire au moins.

2. Le processus de la revendication 1, où le métal alcalin élémentaire est le potassium.
3. Le processus de la revendication 1 ou 2, où le métal alcalin élémentaire est présent en une quantité de 1 à 20 % en poids par rapport au poids total du support.
4. Le processus de l'une des revendications précédentes, où le carbonate de métal alcalin est le carbonate de potassium.
5. Le processus de catalyseur de l'une des revendications 2 à 4, où le carbonate de potassium est présent en une quantité de 85 à 97 % en poids.
6. Un processus pour la préparation d'un support de catalyseur tel que défini dans l'une des revendications 1, 4 ou 5, comprenant :
 - (a) la préparation d'une pâte épaisse comprenant du carbonate de métal alcalin, une silice-alumine vitrifiée à faible surface spécifique et un liquide ;
 - (b) la formation d'un produit particulaire à partir de cette pâte ; et
 - (c) le séchage de ce produit particulaire.
7. Un processus pour produire une composition de catalyseur, qui comprend la mise en contact d'un support tel que défini dans l'une des revendications 1, 4 ou 5 avec au moins un métal alcalin élémentaire.
8. Le processus de la revendication 7, où la mise en contact est opérée dans une atmosphère dépourvue d'oxygène et à une température provoquant la fusion du métal alcalin élémentaire.
9. Le processus de la revendication 7 ou 8, où le métal alcalin élémentaire est tel que défini dans la revendication 2 ou 3.
10. Le processus de l'une des revendications 7 à 9, comprenant en outre la mise en contact du système catalyseur avec au moins un promoteur choisi parmi l'acier inoxydable finement divisé, le cuivre élémentaire, le cobalt élémentaire, le verre finement divisé et leurs mélanges.
11. Le processus de la revendication 6, où le carbonate de métal alcalin est tel que défini dans la revendication 4.
12. Le processus de la revendication 6 ou 11, où le produit particulaire est formé par :
 - (a) séchage de la pâte épaisse de manière à éliminer de cette pâte pratiquement la totalité du liquide de manière à former un produit séché ;
 - (b) broyage du produit séché de l'étape (a) ; et
 - (c) recueil d'un produit particulaire de dimensions de particule essentiellement uniforme.
13. L'utilisation de la composition de catalyseur telle que définie dans l'une des revendications 1 à 5 et 7 à 9 pour la dimérisation des oléfines.
14. L'utilisation de la revendication 13, où la dimérisation comprend une température dans la plage allant de 80 à 200 °C, une pression dans la plage allant de 6,9 à 27,6 MPa et une vitesse spatiale horaire pondérale dans la plage allant de 0,1 à 10, en utilisant des composés oléfiniques ayant de 3 à 30 atomes de carbone.