

Description**BACKGROUND OF THE INVENTION**

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

10 It is known in the art to employ alkali metal carbonate supported alkali metal catalysts for such conversions as propylene dimerization. It is also known in the art to prepare alkali metal carbonate catalyst supports by making a thick paste in a liquid and eventually forming a pelletized, tabletted, or granular support, see EP-A-0 351 748 and EP-A-0 313 050 which both disclose potassium carbonate supports, catalysts and olefin dimerization processes therewith. In these references the catalyst supports are prepared from an alkali metal carbonate, water water soluble ketone (EP-A-0 351 748) and alcohol (EP-A-0 313 050), respectively, and optionally at least one carbonaceous compound. The support prepared in such a manner subsequently can be treated with an elemental alkali metal to form a catalyst system. Alkali metal carbonate catalyst supports prepared from a water-based paste are difficult to process because the alkali metal carbonate to water ratio must be closely controlled or the paste can have the wrong consistency and be unworkable. Additionally, all of the mixing and drying conditions must be carefully controlled in order to form a useable support. Extrusion of an alkali metal carbonate and water paste is much more efficient than forming individual pellets or tablets, but is extremely complex because of either high solubility of higher molecular weight alkali metal carbonates or the low solubility of lower molecular weight alkali metal carbonates in water. Thus, it is difficult to process and easily form a useable catalyst support from an alkali metal carbonate and water.

SUMMARY OF THE INVENTION

25 It is an object of this invention to provide a process to easily prepare a potassium carbonate catalyst support.

It is a further object of this invention to provide an easily processed potassium carbonate catalyst support.

30 It is yet another object of this invention to provide a method to prepare an improved potassium carbonate supported elemental alkali metal catalyst system.

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

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

35 In accordance with the present invention, a potassium carbonate catalyst support is prepared from a thick paste comprising potassium carbonate and water. The resultant thick paste is extruded into an extrudate product, dried, and calcined to give a catalyst support, wherein the water to potassium carbonate weight ratio is from 0.23 to 0.29 grams water per gram potassium carbonate, and potassium carbonate and water are mulled for a time of up to about 60 minutes prior to extrusion and actively mixed for 1 to 50 percent of the total mulling time. Additionally, at least one elemental alkali metal can be contacted with the extruded support to form an olefin dimerization catalyst system.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

45 The present invention provides a process to prepare a catalyst support which comprises the steps of forming a thick paste comprising potassium carbonate and water, and extruding said paste to form an extrudate, wherein the water to potassium carbonate weight ratio is from 0.23 to 0.29 grams water per gram potassium carbonate, and potassium carbonate and water are mulled for a time of up to about 60 minutes prior to extrusion and actively mixed for 1 to 50 percent of the total mulling time. In order to form a catalyst support, the extrudate then must be dried and subsequently calcined.

50 In accordance with yet another embodiment of the invention, the previously prepared extruded potassium carbonate catalyst support can be contacted with at least one elemental alkali metal to produce a catalyst composition which is useful to dimerize olefins.

In accordance with yet a further embodiment of the invention, the potassium carbonate catalyst support and the elemental alkali metal catalyst composition can be contacted with at least one promoter.

Supports

Commercially available potassium carbonate, in the form of, e.g. powder or granules, is mixed with water to form a thick paste. The support must be prepared from potassium carbonate in order to be able to extrude a water/potassium carbonate mixture that forms a useful catalyst support. Other alkali metal carbonates are either too insoluble or too soluble in water to be used easily in an extrusion process. Additionally, a potassium carbonate support is more easily impregnated with an elemental alkali metal than other supports.

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.

In order to be able to extrude a water/potassium carbonate mixture, the final ratio of water to potassium carbonate during the extrusion process is critical. Generally, the mass ratio (gram/gram) during extrusion of water to potassium carbonate is within the range of 0.23 to 0.29, when using dried potassium carbonate, and preferably within the range of 0.24 to 0.28. Most preferably, the water to potassium carbonate weight ratio is within the range of 0.25 to 0.27 grams of water per grams potassium carbonate in order to provide a consistent, durable catalyst support which can be used to obtain high selectivity, high olefin conversion, and a high ratio of desired isomers to undesired isomers.

The water to potassium carbonate ratio during the extrusion process can also be expressed in terms of moles of water per mole of potassium carbonate. Generally a molar ratio within the range of 1.8 (i.e., 1.8 moles of water per mole of potassium carbonate) to 2.2 is used during extrusion; preferably within the range of 1.8 to 2.1. Most preferably, for the reasons given above, a molar ratio of water to potassium carbonate is within a range of 1.9 to 2.1. If too much water is used, the potassium carbonate can completely dissolve and be unextrudable. If too little water is used, the paste will not extrude either because it is too dry or too thick.

Preferably, in order to better control temperature, since the reaction between water and potassium carbonate is exothermic, and to prepare a porous extrudate with an appropriate pore size distribution, the water is pre-mixed with a minor amount of potassium carbonate to form a dilute aqueous potassium carbonate solution prior to contacting the major portion of the potassium carbonate. Any source can be used for the minor amount of potassium carbonate which is pre-mixed with the water. For example, commercially available new potassium carbonate can be used. Other sources include, but are not limited to, catalyst support waste material, i.e., non-useable support material generated during the support preparation process, such as, for example, dried and/or calcined fines; off-specification catalyst support; and/or catalyst support. Usually, the concentration of the dilute potassium carbonate solution is at least about 0.001M (0.001 moles K_2CO_3 /liter H_2O) and preferably within the range of 0.002 M to 0.01 M, for the reasons stated above.

Preferably, although not required, mixing occurs as the liquid, i.e., water, or dilute water/potassium carbonate solution, is being added to the potassium carbonate. The liquid is added to the potassium carbonate in such a manner so as to affect thorough contacting of the water and potassium carbonate. Good liquid/carbonate mixing occurs if the liquid is not poured, but is distributed evenly over the potassium carbonate. Most preferably the liquid is sprayed onto the potassium carbonate for best contacting.

The amount of time used to add the liquid is any amount of time necessary to effect thorough contacting of the liquid and potassium carbonate. However, the liquid addition time can vary with the volume of liquid and mass of potassium carbonate used. For example, when preparing up to about 100 pounds of catalyst support, liquid addition times up to about one hour is sufficient, preferably within the range of 3 to 15 minutes. Most preferably, times within the range of 3 to 6 minutes are used for best mixing and contacting. Faster, more rapid, addition times are preferred so that all of the liquid and potassium carbonate can be contacted nearly simultaneously and, thus, forming a better, more durable, catalyst support.

After the liquid is added to the potassium carbonate, mixing, or mulling occurs. Once again, the mix time can vary with the quantity of potassium carbonate and liquid combined. The mulling time, after all the liquid is added, is up to about 1 hour, and preferably within the time range of 10 minutes to 1 hour. Most preferably, the mixing time is within the range of 10 to 40 minutes, in order to ensure that the potassium carbonate reaction with water is complete, for good extrusion rates, and to give a consistent ratio of desired to undesired isomer products.

Although there is mixing time, the entire mixing time usually is not considered active mixing time. As defined in this disclosure, mixing time is the contact time of liquid and potassium carbonate, i.e., mixer residence time. Active mixing time is the mixing time, expressed in terms of percent, wherein the mixer, or

muller, is actually operating. Usually, the liquid/potassium carbonate is actively mixed for 1 to 50 percent of the time, preferably for 1 to 40 percent of the total mixing time. Preferably, the liquid/potassium carbonate is actively mixed for 5 to 20 percent of the time for good liquid/solid contacting and to maintain potassium carbonate particle integrity.

The temperature of the liquid and newly formed thick paste during the liquid addition and subsequent mixing generally is maintained at or below room temperature, and preferably is within the range of 0° to 10° C. Most preferably, the temperature during mixing is within the range of 0° to 5° C. High temperatures can cause increased dissolution of the potassium carbonate, which can cause the dried extrudate to be less porous, and therefore less suitable as a catalyst support. Low temperatures, i.e., below the freezing point of water, can cause solidification of the thick paste.

After liquid addition and the water/potassium carbonate mulling, the paste optionally can be aged. Generally, aging times of greater than 24 hours do not produce any additional benefits. Preferably, the paste is aged for times within the range of 0 to 8 hours and most preferably for times within the range of 0 to 2 hours. Longer aging times tend to improve extrusion rates, but long aging times also tend to slow production and can be uneconomical.

Once the liquid/potassium carbonate thick paste is prepared, i.e., mulled and, if desired, aged, the thick paste is then ready for extrusion. The paste can be formed into an extrudate using an extruder. The extrudate can be any diameter, but for best catalytic activity and ease of handling and processability, the extrudate is from 1/16 to 1/4 inch in diameter. Larger or smaller diameter extrudates can be prepared, depending on the desired use of the resultant extrudate. After the extrudate passes through the extruder die, the extrudate can be cut into uniform lengths, if desired. However, uniform lengths are not always necessary, so the extrudate can be allowed to break on its own, into any lengths. If the extrudate is allowed to break on its own, it will usually have a length of 2 to 7 times the diameter width. Usually, the extrudate is allowed to break of its own accord because of ease of manufacture and economics.

In order to prepare a catalyst support that can be easier to impregnate with an elemental alkali metal, the barrel temperature of the extruder should be closely controlled. Generally, extruder barrel temperatures within the range of 0° to 60° C are acceptable, although the temperature range can vary based on the subsequent drying process. For example, if the extrudate is to be vacuum dried, extruder barrel temperatures within the range of 10° to 30° C are preferred and most preferably temperatures within the range of 20° to 30° C are used. If a convection drying process is to be used, preferably, the extruder barrel temperatures are within the range of 20° to 60° C, and most preferably within the range of 20° to 50° C. Lower temperatures usually result in easier elemental alkali metal impregnation; higher temperatures can inhibit elemental alkali metal impregnation.

The extrusion rate, expressed in terms of mass of extrudate produced per unit time, i.e., grams (pounds) per minute, depends on many factors, such as, for example, particular equipment used, water level, mixing time, extruder auger speed, and/or aging time. For example, a higher auger speed (expressed in terms of rotations per minute, rpm) will increase the extrusion rate. However, if the auger rpm is too fast or too slow, the extruder can become plugged. Therefore, it is desirable to increase auger rpm, but not at the expense of plugging the extruder and/or producing poor extrudate. When using a large, single screw extruder, such as, for example, a 5.72 cm (2 1/4 inch) Bonnot single screw extruder, the extruder auger rpm is preferably within a range of from 20 to 100 rpm, preferably within a range of from 30 to 80 rpm. Most preferably, for the reasons given above, the extruder auger rpm, when using a large single screw extruder, is within a range of from 45 to 70 rpm.

Once the extrudate is formed, the extrudate can be dried and calcined according to any manner known in the art. Exemplary methods of drying include, but are not limited to, static drying, microwave drying, freeze drying, vacuum drying, and/or convection drying. For ease of use and due to ready availability, vacuum drying and/or convection drying are preferred drying methods.

If vacuum drying of the extrudate is employed, generally the drying temperatures are within the range of 145° to 170° C, and preferably within the range of 145° to 165° C. Most preferably, temperatures within the range of 145° to 160° C are used in order to maintain the integrity of the support. Higher drying temperatures can cause fracturing of the extrudate particles and therefore unacceptable fines, and lower temperatures can result in ineffective moisture removal. Generally, the vacuum drying process is considered complete when the extrudate moisture content is within the range of 0 to 3 weight percent water, based on the total weight of the extrudate, and preferably within the range of 0 to 2 weight percent water. Most preferably, the final moisture content is within the range of 0 to 1 weight percent water in order to facilitate elemental alkali metal impregnation. Too high of a residual moisture content makes the subsequent calcination more difficult, and can inhibit the subsequent elemental alkali metal impregnation.

If convection drying of the extrudate is employed, generally drying temperatures within the range of 100° to 260°C are used, and preferably temperatures within the range of 120° to 230°C are used. Most preferably, temperatures within the range of 145° to 205°C are used in order to maintain the integrity of the support, as well as the reasons regarding vacuum drying. Generally, the convection drying process is considered complete when the extrudate moisture content is within the range of 0 to 10 weight percent water, based on the total weight of the extrudate, and preferably within the range of 0 to 6 weight percent water. Most preferably the final moisture content is within the range of 0 to 3 weight percent water in order to facilitate elemental alkali impregnation. Since drying is more economical than the subsequent step of calcining, preferably as much water as possible is removed during the drying step.

Preferably, the support is convection dried. Convection drying is more economical than vacuum drying. More importantly, the surface of a convection-dried support is different from a vacuum-dried support. A convection-dried support has more large pores penetrating the thick wall, or shell, of the potassium carbonate extrudate at the edge of the extrudate; a vacuum-dried extrudate has far fewer pores. After the subsequent calcination step, the shell of a convection-dried, extruded support seems to disappear, and interior and exterior potassium carbonate particles are nearly indistinguishable; and the surface appears rough, similar to dried foam. The shell of a vacuum-dried, extruded support, after calcination, remains thick and distinct; the surface is smooth except for deep fractures and fissures where the few pores were originally visible. This difference in the surface affects the ease of elemental alkali metal impregnation: A convection-dried support can be easier to impregnate than a vacuum-dried support.

The drying atmosphere can be any type of atmosphere. For ease of use and economics, the preferred drying ambient is air.

After the extrudate is dried, it is then calcined to remove any residual water. Calcining, like drying, can be done in any atmosphere. For ease of use and economics, air is the preferred atmosphere. However, if drying or calcining is done in an inert atmosphere and the support is maintained and stored in an inert atmosphere, the amount of oxygen carried into the elemental alkali metal impregnation step can be reduced, thus making the elemental alkali metal impregnation easier and more efficient. Another optional method to minimize exposure to air and for economic efficiency is to perform the drying and calcining processes in the same apparatus, i.e., the same oven, heater, or dryer.

Calcining temperatures and times are interdependent. For example, higher temperatures require shorter calcination times and lower calcination temperatures require longer heating times. Preferably, for economic reasons, lower temperatures and short calcination times are preferred, when possible. Usually, temperatures within the range of 200° to 400°C are employed for calcination, and preferably temperatures within the range of 230° to 350°C are used. Most preferably, for economic reasons, temperatures within the range of 250° to 350°C are used. The calcination time can be any amount of time sufficient to remove substantially all of the water in the support. Generally, calcination times of up to about 5 hours are sufficient, preferably times within the range of 5 minutes to 3 hours are employed. Most preferably, times within the range of 15 minutes to 3 hours are used.

The potassium carbonate support can contain additional components which do not adversely affect the extrusion process or the subsequent drying or calcining steps. For example, pigments, dyes, processing aids, inert fillers, and/or binders can be added. Graphite, or any form of a carbonaceous compound, should not be added to the support prior to support calcining unless it is fully removed during calcining; a carbonaceous compound can have detrimental effects on the catalyst system. For example, the catalyst system wherein the support contains a carbonaceous compound, can fracture and/or disintegrate during the dimerization process due to formation of carbon-alkali metal intercalation compounds.

Catalysts and Promoters

Catalysts systems employed in the practice of this invention comprise one of the potassium carbonate supports described above, at least one elemental alkali metal catalyst, and optionally one or more of the following additional promoters:

- a carbonaceous compound,
- elemental copper,
- elemental cobalt,
- finely divided stainless steel,
- finely divided glass, and
- mixtures of two or more thereof.

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, binders, and the like.

The alkali metals contemplated to be within the scope of the invention include lithium, sodium, potassium, rubidium, cesium, and mixtures thereof. While the proportion of alkali metal combined with the potassium carbonate support can vary appreciably, generally at least about one weight percent of alkali metal based on the total weight of calcined 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 calcined support is most preferred for most efficient use of reagents, high catalyst activity and selectivity, and ease of catalyst preparation. Potassium is the preferred elemental alkali metal due to its ready availability, good catalytic activity and selectivity, as well as ease and safety in handling.

However, some elemental sodium can be combined with the potassium. The addition of sodium to potassium can be beneficial in that the elemental alkali metal impregnation temperature can be lowered. For example, a mixture of up to about 25 weight percent sodium/75 weight percent potassium does not harm selectivity or activity, but greater than about 25 weight percent sodium can adversely affect the catalyst system. Preferably, if using a sodium/potassium mixture to impregnate the support, the mixture will comprise from 0.01 to 10 weight percent sodium, with the balance being potassium, for the most beneficial effects.

The proportion of optional promoter on the potassium 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. Usually, if the promoter is elemental cobalt or finely divided glass, not more than 50 weight percent will be used. With elemental copper, usually not more than about 30 weight percent will be used and usually not more than about 80 weight percent finely divided stainless steel will be used, all based on the total weight of treated support employed.

The general procedure for preparation of the catalyst systems, after calcining the support, of the invention involves heating the potassium carbonate support to a temperature in the range of 80° to 350° C, preferably slightly above the melting point of the particular alkali metal used, cooling the particulate support and then contacting the particulate support with at least one elemental alkali metal in a dry, oxygen-free atmosphere, such as, for example N₂, Ar, or the like, at a temperature sufficient to cause the alkali metal to melt. 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 alkali metal treated 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 continuously 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, 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 little or no catalytic activity in an olefin dimerization reaction can be used. One example of such an inert substance is glass beads. Another example is potassium carbonate extrudates with no alkali metal.

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, the four normal nonenes and so forth; 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 and 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 and 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, tubular reactors, as are well known in the art can be employed. No special materials of construction are required so that steel, stainless steel, glass-lined reactors, or the like 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 about 69.1 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 3.55 to 13.9 MPa (500 to 2,000 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 40 will be employed. A WHSV of 1 to 30 is

preferred, with 1 to 20 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 examples.

EXAMPLES

Example 1

A) Water and Alcohol Catalyst Support Preparation

Twenty pounds of potassium carbonate (K_2CO_3) (JT Baker, ACS reagent grade) were added to a large Lancaster mix-muller. The amount of water added was adjusted to account for moisture in the K_2CO_3 such that the final mixture had 0.24g H_2O /1g K_2CO_3 . The water was evenly added to the mix-muller over a time of about three (3) minutes. Then, n-propanol (C_3OH_8) (JT Baker, ACS reagent grade) was evenly added to the mix-muller over a time of about 5 minutes, such that the final mixture had 0.16g C_3OH_8 /1g K_2CO_3 . The K_2CO_3 , water and alcohol mixture was mixed for 12 minutes, and then a cycle of 4.5 minutes of no mixing (stand time) and 0.5 minutes of mixing commenced and continued for 35 minutes thereafter.

The paste was fed to a 5.72 cm (2¼ inch) Bonnot single screw extruder, with a barrel temperature of 30°C. The extrudate was 0.32 cm (⅛ inch) diameter. The extrudate was vacuum dried at 157°C (315°F) overnight. The dried extrudate was calcined at 270°C (518°F) for 3 hours, under air, to form a support.

For impregnation, potassium was heated to 75°C and the support was heated 100°C, under an inert atmosphere. Potassium was added to the support, with good mixing. Potassium impregnation, or loading, was 8 weight percent, based on the weight of the calcined support.

B) Water Only Catalyst Support Preparation

The procedure of the Water and Alcohol Catalyst Support Preparation was followed exactly, except for two variations. The water/ K_2CO_3 mixture comprised 0.27g H_2O /1g K_2CO_3 . Secondly, no alcohol (n-propanol) was added to the mixture.

C) Dimerization Reaction

The dimerization of propylene was carried out in a steam heated 316 stainless steel tubular reactor (1.3 x 50.8 cm (½ x 20")). The catalyst system (50 grams) was loaded into the reactor. The contents of the tubular reactor were heated to a reaction temperature of about 160°C, at about 11.14 MPa (1600 psig), and propylene was pumped into the reactor with a weight hourly space velocity of 1.2. 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 chromatography (glc) from each run. Three runs were performed with each type of catalyst. The summarized results represent the average analysis of the last dimerization sample collected from each of the 3 runs (see Table I).

TABLE I

	Propylene Conversion, %	Selectivity to 4MP1, %	4MP1/4MP2
Water & Alcohol Extruded Support	19.8	87.2	16
Water Only Extruded Support	20.3	87.5	17

The data show that there is no substantial difference in dimerization results between the two types of catalyst support preparation procedures. However, the use of alcohol requires additional solvent handling and recovery equipment, as well as significant safety precautions. Therefore, a catalyst support extruded using only water as a solvent is much more preferable for economic, as well as safety reasons.

Example II (Comparative Example)

5 Catalyst support was prepared by adding varying amounts of alkali metal carbonate to a small mix-muller. Sodium carbonate (Fisher, reagent grade) and cesium carbonate (Henley Chemicals, technical grade) were tested. Sodium carbonate (Na_2CO_3) has a solubility in cold water of 7.1g $\text{Na}_2\text{CO}_3/100\text{g H}_2\text{O}$. Cesium carbonate (Cs_2CO_3) has a solubility in cold water of 260.5g $\text{Cs}_2\text{CO}_3/100\text{g H}_2\text{O}$. Potassium carbonate has a solubility in cold water of 112 g $\text{K}_2\text{CO}_3/100\text{g H}_2\text{O}$.

10 The paste was fed to a "BB-Gun Bonnot" single screw extruder, with a barrel temperature of 30°C , through a stainless steel die with 4 holes of 0.32 cm (1/8 inch) diameter. The extrudate was dried in a convection or vacuum oven overnight. The dried extrudate was calcined at 343°C (650°F), under air, for 30 minutes, to form a support.

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The results of the extrusions are listed in Table II.

TABLE II

Run	Alkali Metal Carbonate (XCO_2)	gH ₂ O / g(CO_2)	Extrudability	Drying Process	Dried Crush Strength, kg (lbs.)	Calculated Crush Strength, kg (lbs.)	Comments
201	NaCO_3	0.28	yes	convection	1.35 (4.29)	1.78 (5.93)	extruded fairly well but rough extrudates
202	NaCO_3	0.30	yes	convection	2.44 (5.37)	1.98 (5.25)	extruded fairly well, but rough extrudates
203	CsCO_3	0.26	no, too wet	--	--	--	made syrup-like liquid
204	CsCO_3	0.11	no, too dry	--	--	--	--
205	CsCO_3	0.14	yes, wet	convection ^a	--	--	solid in convection oven
206	CsCO_3	0.11	no, too dry	--	--	--	--
207	CsCO_3	0.14	yes	vacuum	3.52 (7.75)	3.64 (8.02)	extrudate was wet and sticky
208	CsCO_3	0.12	no, too dry	--	--	--	--
209	CsCO_3	0.13	no, too dry	--	--	--	--
210	CsCO_3	0.13	yes	vacuum	2.12 (4.66)	--	about one-half of feed formed extrudates

^a dried at 176°C, for 2 hours

The data in Table II show that sodium carbonate and cesium carbonate can be extruded from a water-only based paste. However, the sodium carbonate extrudates are inferior to potassium carbonate extrudates (see Example IV), in that sodium carbonate extrudates have a rough exterior and have relatively weak crush

strengths. Cesium carbonate extrudates have acceptable crush strengths, compared to potassium carbonate extrudates, but cesium carbonate and water is difficult to extrude and the resultant extrudate cannot be vacuum dried.

5 Example III

Catalyst support was prepared by adding 20 pounds of potassium carbonate (JT Baker, ACS reagent grade) to a large Lancaster mix-muller. The amount of water added was adjusted to account for moisture in the K_2CO_3 , such that the final mixture had 0.28g H_2O/g K_2CO_3 . The water, which had a temperature of 4°C, was evenly added to the mix-muller over a time of about 6 minutes. The total residence time of the K_2CO_3 and water in the mix-muller was 20 minutes after completion of the water addition.

The paste was fed to a 5.72 cm (2¼ inch) Bonnot single screw extruder, with a barrel temperature of 30°C, through a stainless steel die with 48 holes of 0.32 cm (¼ inch) diameter. The extrudate was dried in a convection oven at 177°C (350°F), under air, for 3 hours. The dried extrudate was calcined at 343°C (650°F), under air, for 30 minutes, to form a support.

Catalysts with various levels of elemental sodium and elemental potassium were prepared by weighing out solid sodium and potassium, and then melting them together.

For impregnation, elemental alkali metal(s) was heated to 75°C and the support was heated to 100°C, under an inert atmosphere. The molten elemental alkali metal was added to the support, with good mixing. Elemental alkali metal(s) impregnation, or loading, was 4 weight percent, based on the weight of the calcined support.

The dimerization of propylene was carried out in a steam heated 316 stainless steel tubular reactor (1.3 x 50.8 cm (½ x 20")). The catalyst system (40 grams) was loaded into the reactor and was bounded above and below by a total of about 10g of glass beads. The contents of the tubular reactor were heated to a reaction temperature of about 150°C, at about 11.14 MPa (1600 psig), and propylene was pumped into the reactor with a weight hourly space velocity of 3.75. After about 1.5 hours of reaction time and each one hour thereafter for the following 10 hours, a sample was collected and analyzed by gas liquid chromatography (glc). Three runs were performed with each type of catalyst. The summarized results represent the average analysis of the last dimerization sample collected from each of the three runs (see Table III).

TABLE III

Run	% Na*	% K*	4MP1/4MP2
301	0	100	45
302	10	90	45
303	15	85	37
304	20	80	38
305	25	75	35

*percent by weight, based on the total weight of the Na/K blend

The 4MP1 (4-methylpentene-1) to 4MP2 (4-methylpentene-2) ratio is critical because 4MP2 is undesirable, and is very difficult to separate from 4MP1. The data was obtained from the plots of ratio versus selectivity. By comparing the performance at equal selectivity and conversion, a fair comparison of the effects can be given. A selectivity of about 90% 4MP1 was used because that was an average selectivity.

The data show that at 10% Na/90% K (Run 302) there was no loss of selectivity compared to pure potassium (Run 301). While not wishing to be bound by theory, this is probably due to the exchange of sodium of the elemental alkali metal with potassium ions from the potassium carbonate support producing additional potassium and generating sodium ions. At higher sodium levels, this exchange of sodium with potassium is probably much less effective.

Example IV

The following Example describes the variable (parameter) screening process to determine the dominant variable (parameter) factors and the optimization process of the dominant factors of the catalyst support preparation procedure. Unless otherwise specifically stated, catalyst support was prepared as follows.

Seventy-five pounds of potassium carbonate (K_2CO_3) (JT Baker, ACS reagent grade) were added to a large Lancaster mix-muller. The amount of water added was adjusted to account for moisture in the K_2CO_3 , such that the final mixture had from 0.24g H_2O to 0.28g H_2O per gram K_2CO_3 . The water was evenly added, i.e. sprayed, onto the mix-muller at a rate of 1.2 kg (2.6 lbs) H_2O /min. Water addition temperature ranged from 0°C (32°F), i.e., ice water, to 20°C (68°F) during the screening process and from 0°C (32°F), i.e., ice water, to 4°C (40°F) during the optimization process. The mixing time ranged from 20 to 60 minutes.

The paste was fed to a 5.72 cm (2¼ inch) Bonnot single screw extruder. The extrudate was vacuum or convection dried and then calcined, under air, to form a support.

Tables IV and V, below, give the parameters and ranges, if appropriate, for the variable (parameter) screening (Table IV) and optimization (Table V) analyses.

TABLE IV

Parameter	Experimental Design Limits	
	Low	High
Water to potassium carbonate (dry) ratio	0.25	0.27
Mix-muller roller height above pan (cm) ((inches))	0.64 (0.25)	2.54(1)
Water addition temperature (°C) ((°F))	0 (32)	20 (68)
Mixing time after water addition (minutes)	20	60
% Agitation during mixing	10	100
Covering of prepared paste	No	Yes
Aging after mixing (minutes)	0	120
Die Cooling	No	Yes
5.72 cm (2¼") Bonnot Extruder auger rpm	40	60
Extruder barrel coolant temperature (°C) ((°F))	30 (86)	50 (122)
K-Tron model 7821 mechanical feeder	35	55
Constants		
	Value	
Batch Size (1)	34.1kg (75 lbs.) K_2CO_3	
Water delivery rate	1.2 kg (2.6 lbs)/min.	
Die holes (2)	40 0.32 cm (1/8") diameter holes	
Die thickness	0.64 cm (0.25 inches)	
Convection oven temperature	177°C (350°F)	
Convection drying time (3)	3 hours	
Calcining temperature	343°C (650°F)	
Calcining time	30 minutes	

TABLE V

Parameter	Experimental Design Limits	
	Low	High
Water to potassium carbonate (dry) ratio	0.24	0.28
Mixing time after water addition (minutes)	20	60
% Agitation during mixing	10	100
5.72 cm (2 1/4") Bonnot Extruder auger rpm	40	60
Convection Drying Temperature (°C) ((°F))	121 (250)	232 (450)
Calcining Temperature (°C) ((°F)), (1)	260 (500)	343 (650)
Calcining Time (min.), (2)	30	180
Constants		
Batch Size	Value (75 lbs.) K ₂ CO ₃	
Mix-muller roller height above pan (cm) ((inches))	2.54 (1)	
Water delivery rate	1.2kg (2.6 lbs.)/min.	
Water addition temperature (°C) ((°F))	0-4 (32-40)	
Covering of prepared paste	Yes	
Aging after mixing (min.)	0	
Die Cooling	Yes	
Die holes	48 0.32 cm (1/8") diameter holes	
Die thickness	0.64 cm (0.25 inches)	
Extruder barrel coolant temperature (°C) ((°F))	30 (86)	
K-Iron model 7821 mechanical feeder	55	
Convection oven temperature	177°C (350°F)	
Convection drying time	3 hours	

Notes:

- (1) All samples were calcined at both calcining temperatures.
 (2) All samples were calcined at both calcining times.

A multiple linear regression analysis, Systat®, was performed by computer to determine the dominant variable (parameter) factors. The Systat® computer program is commercially available from Systat, Inc., Evanston, IL.

The dominant variable (parameter) factors analyzed are those listed as "Parameters" in Table IV. Based on the multiple linear regression analysis, the most important variables are:

- 1) H₂O to K₂CO₃ Ratio
- 2) Mixer Residence Time
- 3) Fraction of Active Mixing
- 4) Extruder Auger rpm
- 5) Drying Temperature

These five variables were studied for optimization. The analytical results, in Tables VI and VII below, were also analyzed with Systat®, a multiple linear regression analysis computer program, to determine the true optimization. The data in Table VI provides support and catalyst properties. The data in Table VII provides support and catalyst properties, as well as propylene dimerization process results. The dimerization results were obtained under dimerization conditions similar to those previously described in Example I.

TABLE VI

Run	gH ₂ O/ gK ₂ CO ₃	Mixer Residence Time (min.)	Active Mixing, Z time	Extruder Auger rpm	Drying Temp (°C) (°F)	Z Fines by weight (a)	Bried Crush ₅₀ (c) (kg) (lbm)	Bulk Density (g/cc) (lb/g)	K ₂ CO ₃ Extruded kg (lb)	Extrusion rate kg (lb)/min	Z Fuel (b) Inches	Z Partic (b) Inches	Z No (b) Inches
401	0.26	40	50	50	125 (250)	3.4	4.0 (8.8)	0.72	0.81	0.39 (0.85)	7.5	30	62.5
402	0.27	20	10	60	200 (400)	2.7	2.3 (5.0)	0.47	0.57	0.39 (0.85)	7.5	47.5	45
403 (amb-d)	0.26	40	100	50	175 (350)	4.5	3.6 (8.0)	0.62	0.73	0.39 (0.85)	25	45	30
404	0.26	40	50	60	175 (350)	3.8	3.4 (7.5)	0.67	0.80	0.39 (0.85)	0	0	100
405	0.27	60	10	40	200 (400)	2.9	2.5 (5.4)	0.41	0.54	0.39 (0.85)	0	0	100
406 (amb-d)	0.25	60	100	40	200 (400)	7.4	2.0 (4.5)	0.56	0.64	0.39 (0.85)	27.5	47.5	25
407	0.25	20	10	40	200 (400)	4.1	3.1 (6.8)	0.64	0.74	0.39 (0.85)	32.5	60	7.5
408 (amb-d)	0.26	90	50	50	175 (350)	5.1	3.3 (7.3)	0.59	0.71	0.39 (0.85)	5	27.5	67.5
409 (amb-d)	0.27	60	100	40	100 (200)	3.9	4.0 (8.9)	0.7	0.81	0.39 (0.85)	30	45	10
410 (amb-d)	0.27	60	100	60	200 (400)	5.2	2.5 (5.5)	0.53	0.64	0.39 (0.85)	35	20	20
411 (amb-d)	0.25	20	100	40	175 (350)	5.4	3.1 (6.8)	0.71	0.80	0.39 (0.85)	0	20	80
412 (amb-d)	0.26	20	100	60	175 (350)	4.1	3.5 (7.7)	0.68	0.79	0.39 (0.85)	20	25	55
413 (amb-d)	0.26	60	100	60	175 (350)	8.7	3.2 (6.9)	0.65	0.76	0.39 (0.85)	100	0	0
414	0.26	40	20	50	175 (350)	2.4	3.1 (6.8)	0.47	0.62	0.39 (0.85)	85	15	0
415	0.24	10	50	50	175 (350)	3.4	3.3 (7.3)	0.63	0.71	0.39 (0.85)	65	30	5
416	0.28	40	50	30	175 (350)	4.7	2.6 (5.7)	0.62	0.74	0.39 (0.85)	62.5	35	2.5
417	0.25	40	50	50	175 (350)	8.2	3.2 (7.0)	0.58	0.71	0.39 (0.85)	0	50	0
418	0.28	40	50	50	175 (350)	0	2.5 (5.5)	0.35	0.43	0.39 (0.85)	0	50	0
419	0.25	60	10	60	200 (400)	6.2	2.6 (5.7)	0.6	0.75	0.39 (0.85)	30	70	0
420	0.25	60	10	40	175 (350)	5.3	3.6 (8.0)	0.67	0.80	0.39 (0.85)	25	50	25
421 (amb-d)	0.25	20	100	60	200 (400)	5.4	3.0 (6.7)	0.63	0.74	0.39 (0.85)	55	45	0
422	0.27	20	10	60	175 (350)	3.9	4.1 (9.0)	0.5	0.67	0.39 (0.85)	0	40	40
423	0.27	20	10	40	175 (350)	4.2	3.3 (6.5)	0.67	0.81	0.39 (0.85)	0	20	30
424	0.25	20	10	60	175 (350)	7.0	3.7 (8.2)	0.68	0.78	0.39 (0.85)	75	25	0
425 (amb-d)	0.27	20	100	40	200 (400)	4.1	2.3 (5.1)	0.5	0.61	0.39 (0.85)	40	40	0
426	0.26	40	50	50	232 (465)	5.5	3.0 (6.7)	0.56	0.67	0.39 (0.85)	45	50	5
427	0.26	40	50	55	175 (350)	4.8	3.5 (7.8)	0.61	0.74	0.39 (0.85)	47.5	42.5	10
428 (amb-d)	0.26	40	75	60	175 (350)	5.3	3.2 (6.4)	0.64	0.77	0.39 (0.85)	-	-	-
429	0.26	60	10	60	135 (275)	4.9	4.3 (9.4)	0.72	0.85	0.39 (0.85)	-	-	-

(a) Determined on dried, non-gelatinized support.

(b) Support Calculated at 260°C (500°F) for 30 minutes prior to impregnation.

(c) Fines are those particles that are less than 10 mesh (1.65mm) after extrusion and drying.

TABLE VII

Run	gH ₂ O/ gC ₂ H ₅	Mixer Residence Time (min.)	Active Mixing, Z time	Extruder Auger rpm	Drying Temp (°C)	Z Full Imreg	Z Partia Imreg	Z No Imreg	Propylene Conversion, %	4-MP-1 Selectivity, %	4MP1 to 4MP2 Ratio
430	0.26	40	50	50	(21(250)	40	32.5	27.5	5	87	10.5
431	0.27	20	10	60	209(400)	92.5	5	2.5	25	88	29.0
432 (control)	0.26	40	100	50	172(350)	47.5	40	12.5	-	-	-
433	0.26	40	50	60	172(350)	75	22.5	2.5	30	90	25.4
434	0.27	60	10	40	209(400)	23.5	53.4	23.3	13	87	18.3
435 (control)	0.25	60	100	40	209(400)	27.5	55	17.5	44	89	25.6
436	0.25	20	10	40	209(400)	42.5	45	12.5	20	89	21.5
437 (control)	0.26	90	50	50	172(350)	72.5	27.5	0	36	90	21.1
438 (control)	0.27	60	100	40	143(300)	45	50	5	6	89	25.7
439 (control)	0.27	60	100	60	209(400)	95	15	0	39	88	17.4
440 (control)	0.25	20	100	40	143(300)	70	30	0	20	90	25.9
441 (control)	0.27	20	100	60	143(300)	35	50	15	4	88	25.2
442 (control)	0.25	60	100	60	143(300)	40	30	30	5	88	20.1
443	0.26	40	2	50	172(350)	75	25	0	36	89	17.9
444	0.26	10	50	50	172(350)	82.5	17.5	0	37	88	19.3
445	0.26	40	50	50	172(350)	65	35	0	27	89	21.0
446	0.24	40	50	50	172(350)	65	35	0	40	89	21.7
447	0.28	40	50	50	172(350)	10	60	30	10	89	24.2
448	0.25	60	10	60	209(400)	55	45	0	26	90	22.1
449	0.25	60	10	40	143(300)	55	35	10	5	91	41.4
450 (control)	0.25	20	100	60	209(400)	60	40	0	28	90	23.8
451	0.27	60	10	60	143(300)	40	50	10	11	88	22.8
452	0.27	20	10	40	143(300)	0	20	80	13	89	26.4
453	0.25	20	10	60	143(300)	80	20	0	31	90	20.0
454 (control)	0.27	20	100	40	209(400)	75	25	0	24	89	21.8
455	0.26	40	50	50	232(350)	20	80	0	23	90	26.8
456	0.26	40	50	55	172(350)	10	35	55	40	87	16.0
457 (control)	0.26	40	75	60	172(350)	-	-	-	20	88	24.0
458	0.26	60	10	60	135(275)	-	-	-	10	88	23.4

(a) Support calcined at 343°C (650°F) for 30 minutes prior to impregnation.

The multiple linear regression analysis performed on the experimental data given in Tables VI and VII resulted in optimum conditions needed to perform an efficient extrusion, as well as produce the best overall catalyst and catalyst support. The results, as determined by the Systat® program, given in Table VIII below, are given as ranges in order to account for reasonable deviations from the computer-generated optimized conditions.

TABLE VIII

Parameter	Broad Range	Optimized Range	Computer-Generated Optimized Condition
gH ₂ O/gK ₂ CO ₃	0.23 - 0.29	0.25 - 0.27	0.26
Total mixing time (min.) after initial water addition	up to one (1) hour	20 - 40 min.	20 min.
Active mixing, % time	1 - 50	5 - 20	10%
Extruder auger, rpm	20 - 100	45 - 70	60 rpm
Convection Drying temp., °C (°F)	100 - 260 °C (212 - 500 °F)	145 - 205 °C (293 - 401 °F)	177 °C (350 °F)

While none of the Runs correspond exactly to the computer-generated optimized conditions, Runs 414 and 453 correspond very closely to the computer-generated optimized conditions. The only variances are gH₂O/gK₂CO₃ of 0.25 and drying temperature of 149 °C (300 °F). Runs 414 and 453 show good elemental alkali metal (potassium) impregnation, as well as good propylene conversion, 4MP1 selectivity, and 4MP1/4MP2 ratio.

The examples have been provided merely to illustrate the practice of the invention and should not be read so as to limit the scope of the invention or the appended claims in any way.

Claims

1. A process for preparing a catalyst support comprising preparing a thick paste comprising potassium carbonate and water, extruding said paste to form an extrudate and drying said extrudate as well as, optionally, calcining said dried extrudate, wherein the water to potassium carbonate weight ratio is from 0.23 to 0.29 grams water per gram potassium carbonate, characterized in that said potassium carbonate and water are milled for a time of up to about 60 minutes prior to extrusion and actively mixed for 1 to 50 percent of the total mulling time.
2. The process of claim 1 wherein said potassium carbonate and water are milled at a temperature from 0 to 25 °C.
3. The process of claim 1 or 2 wherein said potassium carbonate and water are aged for a time of up to about 24 hours after mulling.
4. The process of any of the preceding claims wherein said paste is extruded through an extruder with a barrel temperature from 0 to 60 °C.
5. The process of any of the preceding claims wherein said drying is a vacuum drying process.
6. The process of claim 5 wherein said vacuum drying is done at a temperature from 145 to 170 °C.
7. The process of claim 5 or 6 wherein the vacuum-dried extrudate comprises up to about 3 weight percent water, based on the total weight of the extrudate.
8. The process of any of claims 1-4 wherein said drying is a convection drying process.
9. The process of claim 8 wherein said convection drying process is done at a temperature from 100 to 260 °C.
10. The process of claim 8 or 9 wherein the convection-dried extrudate comprises up to about 10 weight percent water, based on the total weight of the extrudate.
11. The process of any of the preceding claims wherein said calcining occurs at a temperature from 260 to 400 °C.



TABLE VIII

Parameter	Broad Range	Optimized Range	Computer-Generated Optimized Condition
gH ₂ O/gK ₂ CO ₃	0.23 - 0.29	0.25 - 0.27	0.26
Total mixing time (min.) after initial water addition	up to one (1) hour	20 - 40 min.	20 min.
Active mixing, % time	1 - 50	5 - 20	10%
Extruder auger, rpm	20 - 100	45 - 70	60 rpm
Convection Drying temp., °C (°F)	100 - 260 °C (212 - 500 °F)	145 - 205 °C (293 - 401 °F)	177 °C (350 °F)

While none of the Runs correspond exactly to the computer-generated optimized conditions, Runs 414 and 453 correspond very closely to the computer-generated optimized conditions. The only variances are gH₂O/gK₂CO₃ of 0.25 and drying temperature of 149 °C (300 °F). Runs 414 and 453 show good elemental alkali metal (potassium) impregnation, as well as good propylene conversion, 4MP1 selectivity, and 4MP1/4MP2 ratio.

The examples have been provided merely to illustrate the practice of the invention and should not be read so as to limit the scope of the invention or the appended claims in any way.

Claims

1. A process for preparing a catalyst support comprising preparing a thick paste comprising potassium carbonate and water, extruding said paste to form an extrudate and drying said extrudate as well as, optionally, calcining said dried extrudate, wherein the water to potassium carbonate weight ratio is from 0.23 to 0.29 grams water per gram potassium carbonate, characterized in that said potassium carbonate and water are mulled for a time of up to about 60 minutes prior to extrusion and actively mixed for 1 to 50 percent of the total mulling time.
2. The process of claim 1 wherein said potassium carbonate and water are mulled at a temperature from 0 to 25 °C.
3. The process of claim 1 or 2 wherein said potassium carbonate and water are aged for a time of up to about 24 hours after mulling.
4. The process of any of the preceding claims wherein said paste is extruded through an extruder with a barrel temperature from 0 to 60 °C.
5. The process of any of the preceding claims wherein said drying is a vacuum drying process.
6. The process of claim 5 wherein said vacuum drying is done at a temperature from 145 to 170 °C.
7. The process of claim 5 or 6 wherein the vacuum-dried extrudate comprises up to about 3 weight percent water, based on the total weight of the extrudate.
8. The process of any of claims 1-4 wherein said drying is a convection drying process.
9. The process of claim 8 wherein said convection drying process is done at a temperature from 100 to 260 °C.
10. The process of claim 8 or 9 wherein the convection-dried extrudate comprises up to about 10 weight percent water, based on the total weight of the extrudate.
11. The process of any of the preceding claims wherein said calcining occurs at a temperature from 260 to 400 °C.



12. The process of claim 1, characterized by

- (a) preparing a thick paste comprising potassium carbonate and water, wherein the water to potassium carbonate weight ratio is about 0.29 grams water per gram potassium carbonate;
- (b) mixing said thick paste for a time of up to 60 minutes, wherein said thick paste is actively mixed for 1 to 50 percent of the total mixing time, at a temperature from 0 to 25 °C;
- (c) extruding said paste through an extruder to form an extrudate, wherein said extruder barrel temperature is from 0 to 60 °C;
- (d) drying said extrudate at a temperature from 100 to 260 °C to obtain a dried extrudate comprising up to about 10 weight percent water, based on the total weight of the extrudate; and
- (e) calcining the thus-dried extrudate at a temperature from 260 to 400 °C.

13. The process of any of the preceding claims comprising contacting the calcined extrudate with at least one elemental alkali metal to produce a catalyst system.

14. The process of claim 13 wherein said elemental alkali metal is selected from lithium, sodium, potassium, rubidium, cesium, and mixtures thereof, preferably sodium, potassium, and mixtures thereof.

15. The process of claims 13 or 14 wherein said elemental alkali metal comprises from 1 to 20 weight of the catalyst system, based on the weight of the support.

16. The use of the catalyst system as defined in any of claims 13 to 15 for the dimerization of olefins.

17. A process for the dimerization of olefinic compounds comprising contacting olefinic compounds having from 3 to 30 carbon atoms per molecule with the catalyst system as defined in any of claims 13 to 15, wherein said dimerization is carried out at a temperature from 80 to 200 °C, a pressure from 6.9 to 27.6 MPa, and a weight hourly space velocity from 0.1 to 10.

18. The use of claim 16 wherein propylene is dimerized to 4-methyl-1-pentene.

Patentansprüche

1. Verfahren zur Herstellung eines Katalysator-Trägers, umfassend das Herstellen einer dicken Paste mit einem Gehalt an Kaliumcarbonat und Wasser, das Extrudieren dieser Paste unter Bildung eines Extrudats und das Trocknen dieses Extrudats sowie gegebenenfalls das Calcinieren des getrockneten Extrudats,

wobei das Gewichtsverhältnis von Wasser zu Kaliumcarbonat 0,23 bis 0,29 g Wasser pro g Kaliumcarbonat beträgt,

dadurch gekennzeichnet, daß das Kaliumcarbonat und Wasser vor der Extrusion für eine Zeitspanne bis zu etwa 60 Minuten einem Koller-Mischvorgang unterzogen und für 1 bis 50 % der gesamten Kollermischzeit aktiv vermischt werden.

2. Verfahren nach Anspruch 1, wobei Kaliumcarbonat und Wasser bei einer Temperatur von 0 bis 25 °C dem Koller-Mischvorgang unterzogen werden.

3. Verfahren nach Anspruch 1 oder 2, wobei Kaliumcarbonat und Wasser nach dem Koller-Mischvorgang für eine Zeitspanne bis zu etwa 24 Stunden gealtert werden.

4. Verfahren nach einem der vorstehenden Ansprüche, wobei die Paste durch einen Extruder mit einer Zylindertemperatur von 0 bis 60 °C extrudiert wird.

5. Verfahren nach einem der vorstehenden Ansprüche, wobei es sich bei der Trocknung um ein Vakuum-Trocknungsverfahren handelt.

6. Verfahren nach Anspruch 5, wobei die Vakuumtrocknung bei einer Temperatur von 145 bis 170 °C durchgeführt wird.

7. Verfahren nach Anspruch 5 oder 6, wobei das vakuumgetrocknete Extrudat bis zu etwa 3 Gew.-% Wasser, bezogen auf das Gesamtgewicht des Extrudats, enthält.



8. Verfahren nach einem der Ansprüche 1 bis 4, wobei es sich bei der Trocknung um ein Konvektionstrocknungsverfahren handelt.

9. Verfahren nach Anspruch 8, wobei das Konvektionstrocknungsverfahren bei einer Temperatur von 100 bis 260 °C durchgeführt wird.

10. Verfahren nach Anspruch 8 oder 9, wobei das durch Konvektionstrocknung getrocknete Extrudat bis zu etwa 10 Gew.-% Wasser, bezogen auf das Gesamtgewicht des Extrudats, enthält.

11. Verfahren nach einem der vorstehenden Ansprüche, wobei die Calcinierung bei einer Temperatur von 260 bis 400 °C erfolgt.

12. Verfahren nach Anspruch 1, gekennzeichnet durch

(a) Herstellen einer dicken Paste mit einem Gehalt an Kaliumcarbonat und Wasser, wobei das Gewichtsverhältnis von Wasser zu Kaliumcarbonat etwa 0,29 g Wasser pro g Kaliumcarbonat beträgt;

(b) Vermischen der dicken Paste für eine Zeitspanne bis zu 60 Minuten, wobei die dicke Paste 1 bis 50 % der gesamten Mischzeit bei einer Temperatur von 0 bis 25 °C aktiv vermischt wird;

(c) Extrudieren der dicken Pasten durch einen Extruder unter Bildung eines Extrudats, wobei die Extruder-Zylindertemperatur 0 bis 60 °C beträgt;

(d) Trocknen des Extrudats bei einer Temperatur von 100 bis 260 °C unter Bildung eines getrockneten Extrudats, das bis zu etwa 10 Gew.-% Wasser, bezogen auf das Gesamtgewicht des Extrudats, enthält; und

(e) Calcinieren des auf diese Weise getrockneten Extrudats bei einer Temperatur von 260 bis 400 °C.

13. Verfahren nach einem der vorstehenden Ansprüche, umfassend das Kontaktieren des calcinierten Extrudats mit mindestens einem elementaren Alkalimetall unter Bildung eines Katalysatorsystems.

14. Verfahren nach Anspruch 13, wobei das elementare Alkalimetall unter Lithium, Natrium, Kalium, Rubidium, Cäsium und Gemischen davon und vorzugsweise unter Natrium, Kalium und Gemischen davon ausgewählt wird.

15. Verfahren nach Anspruch 13 oder 14, wobei das elementare Alkalimetall 1 bis 20 Gew.-% des Katalysatorsystems, bezogen auf das Gewicht des Trägers, ausmacht.

16. Verwendung des in einem der Ansprüche 13 bis 15 definierten Katalysatorsystems zur Dimerisation von Olefinen.

17. Verfahren zur Dimerisation von olefinischen Verbindungen, umfassend das Kontaktieren von olefinischen Verbindungen mit 3 bis 30 Kohlenstoffatomen pro Molekül mit dem Katalysatorsystem gemäß der Definition in einem der Ansprüche 13 bis 15, wobei die Dimerisation bei einer Temperatur von 80 bis 200 °C, einem Druck von 6,9 bis 27,6 MPa und einer auf das Gewicht bezogenen Raumgeschwindigkeit pro Stunde von 0,1 bis 10 durchgeführt wird.

18. Verwendung nach Anspruch 16, wobei Propylen zu 4-Methyl-1-penten dimerisiert wird.

Revendications

1. Un procédé pour préparer un support de catalyseur comprenant la préparation d'une pâte épaisse comprenant du carbonate de potassium et de l'eau, l'extrusion de ladite pâte pour former un extrudat et le séchage dudit extrudat ainsi que, éventuellement la calcination dudit extrudat séché, dans lequel le rapport pondéral eau:carbonate de potassium est de 0,23 à 0,29 grammes d'eau par gramme de carbonate de potassium, caractérisé en ce que ledit carbonate de potassium et ladite eau sont amenés à l'état de pâte pendant une durée allant jusqu'à environ 60 minutes avant l'extrusion et sont mélangés activement pour 1 à 50% de la durée de mise à l'état de pâte totale.



2. Le procédé selon la revendication 1, dans lequel ledit carbonate de potassium et l'eau sont amenés à l'état de pâte à une température de 0 à 25 °C.
- 5 3. Le procédé selon la revendication 1 ou 2, dans lequel ledit carbonate de potassium et l'eau sont vieillissent pendant une durée allant jusqu'à environ 24 heures après la mise à l'état de pâte.
4. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ladite pâte est extrudée à travers une extrudeuse avec une température du cylindre de 0 à 60 °C.
- 10 5. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit séchage est un procédé de séchage sous vide.
6. Le procédé selon la revendication 5, dans lequel ledit séchage sous vide est réalisé à une température de 145 à 170 °C.
- 15 7. Le procédé selon la revendication 5 ou 6, dans lequel ledit extrudat séché sous vide comprend jusqu'à environ 3% en poids d'eau, calculé sur le poids total de l'extrudat.
- 20 8. Le procédé selon l'une quelconque des revendications 1 à 4, dans lequel le séchage est un procédé de séchage par convection.
9. Le procédé selon la revendication 8, dans lequel ledit procédé de séchage par convection est réalisé à une température de 100 à 260 °C.
- 25 10. Le procédé selon la revendication 8 ou 9, dans lequel l'extrudat séché par convection renferme jusqu'à environ 10% en poids d'eau, calculé sur le poids total de l'extrudat.
- 30 11. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ladite calcination est produite à une température de 260 à 400 °C.
- 35 12. Le procédé selon la revendication 1, caractérisé par:
- (a) la préparation d'une pâte épaisse comprenant du carbonate de potassium et de l'eau où le rapport pondéral de l'eau:carbonate de potassium est d'environ 0,29 gramme d'eau par gramme de carbonate de potassium ;
- (b) le mélange de ladite pâte épaisse pendant une durée allant jusqu'à 60 minutes où ladite pâte épaisse est mélangée activement pour 1 à 50% de la durée de malaxage totale à une température de 0 à 25 °C ;
- (c) l'extrusion de ladite pâte à travers une extrudeuse pour former un extrudat où la température du cylindre de l'extrudeuse est de 0 à 60 °C ;
- 40 (d) le séchage dudit extrudat à une température de 100 à 260 °C pour obtenir un extrudat séché comprenant jusqu'à environ 10% en poids d'eau sur la base du poids total de l'extrudat et,
- (e) la calcination de l'extrudat ainsi séché à une température de 260 à 400 °C.
- 45 13. Le procédé selon l'une quelconque des revendications précédentes comprenant la mise en contact de l'extrudat calciné avec au moins un métal alcalin élémentaire pour produire un système de catalyseur.
- 50 14. Le procédé selon la revendication 13, dans lequel ledit métal alcalin élémentaire est choisi parmi le lithium, le sodium, le potassium, le rubidium, le césium et leurs mélanges, de préférence le sodium, le potassium et leurs mélanges.
- 55 15. Le procédé selon la revendication 13 ou 14, dans lequel ledit métal alcalin élémentaire comprend de 1 à 20% en poids du système de catalyseur sur la base du poids du support.
16. L'utilisation du système de catalyseur comme défini dans l'une quelconque des revendications 13 à 15, pour la dimérisation d'oléfines.
17. Un procédé pour la dimérisation de composés oléfiniques comprenant la mise en contact de composés oléfiniques ayant de 3 à 30 atomes de carbone par molécule avec un système de catalyseur comme



défini dans l'une quelconque des revendications 13 à 15, dans lequel ladite dimérisation est mise en oeuvre à une température de 80 à 200 °C, une pression de 6,9 à 27,6 MPa, et une vitesse spatiale horaire pondérale de 0,1 à 10.

- 5 18. L'utilisation selon la revendication 16, dans laquelle du propylène est dimérisé en 4-méthyl-1-pentène.

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