

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

Process for the Catalytic Conversion of Unsaturated Hydrocarbons

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The invention relates to a process for the catalytic conversion of olefinic hydrocarbons by polymerization, alkylation or isomerization reaction and more particularly for the catalytic polymerization of olefinic hydrocarbons.

The need for crude rubber, either natural or synthetic has increased at a tremendous rate inasmuch as rubber has attained a position of great importance as a material of modern manufacture by reason of the diverse uses to which rubber may be put. Since the sources of natural rubber are limited there is an ever growing need for synthetic rubber-like materials. Heretofore, synthetic rubbers such as, for example, the types produced by the reaction of butadiene and styrene (GR-S), butadiene and acrylonitrile (Buna-M), butadiene and isobutylene, Thiokol rubber, silicone rubber, and Neoprene rubber, have been prepared. However, these products have often been inferior to natural rubber in many of the necessary properties when in the vulcanized, elastic state.

The recent discovery that a diolefinic hydrocarbon such as isoprene may be caused to polymerize stereoselectively to a rubbery product similar in many respects to the natural Hevea type rubber (that is a rubbery product of great utility in the manufacture of a rather extensive series of soft and hard rubber goods needed in industry and commerce) has greatly magnified the present

need for a diolefinic hydrocarbon such as isoprene for the production of such a 45 rubber.

It has now been discovered that unsaturated hydrocarbons, particularly olefinic hydrocarbons are amenable to selective conversion in the presence of a novel catalyst hereinafter set forth and, especially, that propylene may be selectively converted in the presence of such catalyst to form a dimer of propylene, namely, 2-methyl-2-pentene, which is an intermediate in the preparation of isoprene, since the demethylation of this 55 ~~propylene~~ dimer produces isoprene.

It is therefore an object of this invention to provide a process for the conversion of unsaturated hydrocarbons using a novel catalyst therefor. Another object of this invention is to provide a process for selectively converting olefinic hydrocarbons to preferred polymers thereof. A specific object of this invention is to provide a process for 65 selectively polymerizing low molecular olefinic hydrocarbons to provide a desired dimer of the olefinic hydrocarbon.

The process according to this invention comprises catalyzing the conversion of an olefinic hydrocarbon by an alkali metal amide comprising a compound of the formula MNH_2 , wherein M is an alkali metal, N is nitrogen and H is hydrogen, disposed on a promoted support consisting essentially of a substantially anhydrous metal oxide having a surface area of from 25 to 500 square meters per gram, said support having been promoted by compositing a small quantity of an alkali metal or an alkaline earth metal on a compound of one of said metals with said metal oxide prior to the disposal of said alkali metal amide thereon.

In one embodiment of this invention an olefinic hydrocarbon is subjected to a con-

[Price 4s. 6d.]



Propylene

densation reaction at a temperature substantially in the range of from 50° to 300°C. and at a pressure in the range of from about 5 to 250 atmospheres in the presence of an animated metal of the group of sodium and potassium disposed on promoted substantially anhydrous alumina having a surface area of from 100 to 300 square meters per gram, said alumina having been promoted by compositing with an oxide of a metal of the group of lithium, sodium, potassium, rubidium and cesium. In accordance with this embodiment 2-methyl-2-pentene is produced advantageously by polymerizing propylene in the presence of aminated potassium disposed on gamma alumina which has been promoted by lithium oxide.

Improved yields of a desired condensed hydrocarbon are obtained in accordance with this invention in another embodiment which comprises passing an olefinic hydrocarbon to a first reaction zone and therein subjecting this hydrocarbon to a condensation reaction in the presence of the alkali metal amide disposed on the promoted metal oxide support, passing the effluent from the first reaction zone to a first separation zone wherein unreacted olefinic hydrocarbon is removed, passing the hydrocarbons formed by the condensation reaction to a second separation zone and therein separating them into desired and undesired isomers, removing the desired isomeric product from the process, passing the undesired isomeric product to a second reaction zone and therein subjecting said undesired isomeric reaction product to isomerization in the presence of an alkali metal amide comprising a compound of the formula MNH_2 wherein M is an alkali metal, N is nitrogen and H is hydrogen, disposed on a promoted support, essentially consisting of a substantially anhydrous metal oxide having a surface area of from 25 to 500 square meters, said support having been promoted by compositing a small quantity of an alkali metal or an alkaline earth metal or a compound of one of said metals with said metal oxide prior to the disposal of said alkali metal amide thereon, and recovering desired isomeric product from the effluent of the second reaction zone. In this embodiment the condensation reaction in the first reaction zone is effected advantageously at a temperature substantially in the range of from 75° to 250°C. and at a pressure of from about 34 to about 136 atmospheres while the undesired isomeric product is isomerized in the second reaction zone preferably at a temperature substantially in the range of from 0° to 75°C. and at a pressure in the range of from about atmospheric to about 136 atmospheres, and preferably in the presence of aminated potassium disposed on a gamma-alumina support promoted by lithium oxide.

A further embodiment of the invention comprises passing an olefinic hydrocarbon to a reaction zone and therein subjecting it to a condensation reaction in the presence of a diluent and an alkali metal amide disposed on a promoted support essentially consisting of a promoted substantially anhydrous metal oxide having a surface area of from 25 to 500 square meters per gram, passing the effluent from this reaction zone to a first separation zone wherein unreacted olefinic hydrocarbon is removed, passing the hydrocarbons formed by the condensation reaction to a second separation zone, and therein separating and recovering the desired hydrocarbon product from a lower boiling undesired product and recirculating this undesired product to the reaction zone as diluent. In accordance with this embodiment of the invention a desired dimer of propylene is produced advantageously by treating propylene in the reaction zone at a temperature substantially in the range of from 50° to 250°C. and at a pressure of from about 48 to about 136 atmospheres in the presence of the supported aminated alkali metal, separating unreacted propylene from the effluent of the reaction zone in the first separation zone and returning this unreacted propylene to the reaction zone, separating the desired propylene dimer such as 2-methyl-2-pentene in the second separation zone to the reaction zone.

Yet another embodiment of this invention resides in the copolymerization of unsaturated hydrocarbons which comprises treating a mixture of unsaturated hydrocarbons of dissimilar configuration at a temperature substantially in the range of from 50° to 250°C. and at a pressure in the range of from about 34 to about 136 atmospheres in the presence of a diluent and an aminated alkali metal disposed on a promoted support essentially consisting of alkalized substantially anhydrous metal oxide having a surface area of from 25 to 500 square meters per gram, and recovering a copolymer from the resultant reaction product. In accordance with this embodiment heptenes are produced advantageously by copolymerizing propylene and butylene in the presence of *n*-pentane as diluent and in the presence of aminated potassium disposed on a promoted gamma-alumina support.

In a further embodiment of this invention, moreover, an unsaturated hydrocarbon which does not possess a primary allylic hydrogen atom is passed to a reaction zone and subjected therein to a condensation reaction in the presence of a diluent and an aminated alkali metal disposed on a promoted support essentially consisting of alkalized substantially anhydrous metal oxide having a surface area of from 25 to 500 square meters per gram, and the effluent

and removing it from the process and recycling lower boiling propylene dimer from the second separating zone

from this zone is passed to a separation zone wherein the condensation reaction product is separated and recovered. In accordance with this embodiment butene-1 is advantageously dimerized by commingling it with normal pentane, subjecting the hydrocarbon mixture in the reaction zone at a temperature substantially in the range of from 50° to 250°C. and at a pressure of from about 34 to about 170 atmospheres to contact with the supported aminated alkali metal and separating the resultant octenes from the effluent of the reaction zone by fractionation in the separation zone.

The terms "condensed" and "condensation" as used herein in the specification and appended claims signify particularly "polymerized" and "polymerization" but are not limited thereto and may also include "alkylation" and "isomerization." The term "alkinous metal" as used herein refers to metals of the group including both the alkali metals and the alkaline earth metals, namely lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium and barium. The term "aminated alkali metal" as used herein refers both to alkali metals which have been subjected to amination by reaction with ammonia and to alkali metal amides. The terms "alkalized" and "promoted" as used herein with reference to the catalyst refer to a pretreatment of the metal oxide component of the catalyst support with alkinous metal or an alkinous metal compound prior to the disposal of any aminated alkali metal on the support.

Unsaturated hydrocarbons and particularly olefinic hydrocarbons which may be condensed in the present process include mono-olefins such as ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methylpentenes, 1-hexene, 2-hexene, 3-hexene, methylhexenes, 1-heptene, 2-heptene, and dimethylhexenes; polyolefins such as 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, 1,4-hexadiene and 2-methyl-1,3-hexadiene; cyclic olefins such as cyclopentene, cyclohexene and cycloheptene. The aforementioned olefins may be condensed by themselves. Olefins of the types listed above, moreover, may be condensed with a dissimilar olefin in the present process. Typical olefinic hydrocarbons which do not possess a primary allylic hydrogen and which may be condensed in the present process are ethylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, 4-methylhexene-1, heptene-1, 4-methylheptene-1, octene-1, cyclopentene, cyclohexene and cycloheptene. In addition to the condensation of the aforementioned olefins the present process may be used also for the side chain alkylation of alkyl aromatic hydrocarbons which contain at least one replaceable hydrogen atom on the carbon atom in the side chain, such compounds including toluene, o-xylene, m-xylene, p-xylene, ethyl benzene, propyl benzene, isopropyl benzene, butyl benzene, the diethyl benzenes, and the dipropyl benzenes, the aforementioned olefinic hydrocarbons being used as the alkylation agents. Furthermore an isomerization treatment may be applied in the present process to shift the double bond of unsaturated hydrocarbons, such as, for example, propylene dimer (2-methyl-1-pentene), usually to a more centralized position in the chain without further polymerization of the olefin, the isomerization involving only the shift of the double bond without carbon skeleton rearrangement.

As hereinbefore set forth the conversion process of the present invention is effected in the presence of an aminated alkali metal disposed on an alkalinized metal oxide support. Of the alkali metals which are aminated, potassium and sodium are preferred, inasmuch as these two metals exhibit substantially more activity than do other metals of the alkinous metal group, and potassium is especially preferred for the same reason. In addition to their high activity the aminated sodium and aminated potassium are preferred from an economic standpoint inasmuch as sodium and potassium are relatively more plentiful and correspondingly less expensive to use. The aminated alkali metals are disposed on the promoted support in a quantity ranging from about 2 to about 20% or more by weight (calculated as metal) based on the support.

Not every solid support can be utilized as a satisfactory one for disposal of an alkali metal or aminated alkali metal thereon. As is well known to one experienced in the art, the alkali metals or alkali metal amides react relatively violently with water and thus care must be taken to utilize those supports which are substantially free from water. In most cases, this freedom from water of the support is achieved by a precalcination treatment of the support. This precalcination is carried out at a relatively high temperature in the range of from about 400° to about 700°C. and for a time sufficient to effect substantial removal of adsorbed or combined water from the support. The time required will vary depending upon the support, and in addition depending upon whether the water is in a combined or in merely a physically adsorbed form. In addition to the necessity for freedom from water, the support is characterized by the necessity for having a high surface area. By the term high surface area is meant a surface area measured by surface absorption techniques within the range of from 25 to 500 square meters per

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gram. A support having a surface area of approximately 100 to 300 square meters per gram is preferred. For example, it has been found that certain low surface area supports such as alpha-alumina which is obviously free from combined water and which has been freed from absorbed water is not a satisfactory support for the alkali metals in the preparation of catalysts for use in the process of this invention. Alpha-alumina is usually characterized by a surface area ranging from about 10 to about 25 square meters per gram. In contrast, gamma-alumina which has a surface area ranging from about 100 to about 300 square meters per gram, and which has been freed from absorbed water and which contains little combined water, is a satisfactory support. Celite, a naturally occurring mineral, after precalcination, is not a satisfactory support. Celite has a surface area of from about 2 to about 10 square meters per gram. Likewise alkali metal dispersions on sand or on other low surface area silica are not satisfactory catalysts in this process. In addition, aluminas which contain combined water but which have relatively high surface areas are also not satisfactory supports. Such aluminas include dried alumina mono-hydrates which have not been sufficiently calcined to remove combined water and to form gamma-alumina. These alumina hydrates may have surface areas ranging from about 50 to about 200 square meters per gram but are not satisfactory supports because they have a substantial content of combined water. Particularly preferred supports for the preparation of catalysts for use in the process of this invention include high surface area crystalline alumina modifications such as gamma-, eta- and theta-alumina, although these are not necessarily of identical suitability. However, as is apparent from the above discussion the limitation on the use of any particular support is one of substantial freedom from combined or absorbed water in combination with the surface area of the support selected. In addition to the aforementioned types of suitable support another type is that which is prepared from an alkali aluminate such as sodium aluminate and potassium aluminate, from which a substantial majority of the alkali metal has been removed leaving only the aluminate with a relatively minor amount of the alkali metal present.

The desired support of the type set forth above may be alkalinized or pretreated with a promoter in any manner. One manner of pretreating the support is vaporization of the alkali metal and the passage of the vapors over the support. In this manner of preparation care must be taken to utilize relatively low temperatures since heat is given off on contact of the alkali metal with the

support and since high temperatures tend to destroy the amount of surface in the support, and may also cause chemical reaction of the support with the alkali metal to an extent which is detrimental to catalyst activity. Sodium melts at about 97°C. and in impregnating a selected support with sodium it is preferred to carry out the impregnation or disposal of the sodium thereon at temperatures in the order of from about 100° to about 150°C., that is substantially from 3° to 53°C. above the melting point of the alkali metal. This can be accomplished for example, by melting sodium and by dropping the sodium on the support or by the passage of a stream of inert gas such as nitrogen or argon through the molten sodium and over a bed of the selected support disposed in a separate zone maintained at the desired temperature with cooling or heating means connected therewith. Potassium melts at about 62°C. and thus the impregnation of a selected support with potassium can be carried out at even lower temperatures than those required with molten sodium. Potassium disposed on one of the above mentioned supports appears to yield a more active catalyst for the reactions disclosed herein than does sodium and this difference in activity may be due to the lower temperatures which can be used in the disposal of potassium on the support. Furthermore, disposal of the selected alkali metal on the support must be carried out in a manner so that the high surface of the support in combination with the alkali metal is not destroyed by incorporation of excess quantities of the alkaline metal. This is obviously undesirable and supported aminated alkali metals containing excess alkali metal are relatively inactive in this process.

The support may also be promoted by impregnating it with an alkalizing agent such as a compound of an alkali metal which, on calcination, is decomposed to the oxide. Examples of compounds suitable for this purpose include the hydroxides of the alkali metals such as potassium hydroxide, sodium hydroxide, lithium hydroxide, rubidium hydroxide, and cesium hydroxide. Hydrides such as sodium hydride, potassium hydride, lithium hydride, rubidium hydride, and cesium hydride may also be used as alkalizing agents.

A preferred method of promoting the support is to contact or impregnate the support with the salt or hydroxide of an alkaline metal. A particularly effective salt which may be utilized is a nitrate such as sodium nitrate, potassium nitrate, lithium nitrate, cesium nitrate, barium nitrate, calcium nitrate, magnesium nitrate, and strontium nitrate. Other salts of alkali or alkaline earth metals which will decompose at temperatures below about 750°C. may also be



imp. metal
utilized. If this method of impregnating the solid support is utilized the support is preferably calcined at a temperature in the range of from about 500° to about 5 750°C. whereby the alkinous metal compound is decomposed with formation of an oxide.

contacting
After the support has been promoted as described above it may be impregnated with an alkali metal which is subsequently aminated with ammonia such as potassium, lithium, sodium, cesium or rubidium, in a manner similar to that hereinabove set forth in reference to the pretreatment of the support, namely by vaporizing the alkali metal and contacting the promoted support with the alkali metal vapors, or by treating the promoted support with molten alkali metal, and subsequently aminating with ammonia.

20 After the impregnation of the promoted support such as alkalized alumina with the alkali metal this metal on the support may be aminated by treatment with anhydrous ammonia at temperatures ranging from about 25 25° to about 200°C., the temperature used being dependent on the alkali metal and being preferably maintained below the melting point of the alkali metal. Alternatively the promoted support may be directly impregnated with an aminated alkali metal such as potassium amide, lithium amide, sodium amide, or cesium amide, or with a mixture of the alkali metal amide and metallic alkali metal such as a mixture of potassium amide and metallic potassium, sodium amide and metallic sodium, or lithium amide and metallic lithium.

1,
In treating the promoted metal oxide support with an alkali metal which is subsequently aminated, in one method of preparing the desired catalyst it has been discovered that merely impregnating the solid support with the metallic alkali metal, even with vigorous stirring of the support and the metal, results in a relatively poor distribution of the alkali metal on the metal oxide support. This will result in a catalyst which possesses a relatively low activity as concerns the ability to convert the hydrocarbons to the desired product. The catalytic activity of the catalyst depends not only upon the percentage of aminated alkali metal distributed on the surface of the metal oxide support but also on the uniformity of distribution of the alkali metal prior to amination during the preparation of the catalyst, and it has been established that once the alkali metal has been distributed on the support, it cannot be redistributed merely by heating the support and metal above the melting point and subjecting the molten catalyst to further stirring. Catalysts which possess a relatively high hydrocarbon conversion activity and especially the ability to 65 polymerize unsaturated organic hydrocar-

bons such as olefins and diolefins, and also to promote the isomerization of olefinic hydrocarbons, may be prepared by depositing or impregnating the alkali metal amide on the promoted metal oxide support out of a liquid ammonia solution. When the metal amide is deposited on the promoted metal oxide support while this support is immersed in a liquid ammonia solution at a temperature approximately that of the reflux temperature of ammonia, -33°C., accompanied with vigorous stirring or rotation, the solution is in effect a molecular dispersion and the metal amide which is deposited on the promoted metal oxide support is in an extremely uniform and finely divided state, thereby yielding catalysts which possess a relatively high activity and corresponding ability to catalyze the conversion of the unsaturated hydrocarbons to the desired conversion products, one example of this being the dimerization of propylene to form 2-methyl-2-pentene.

It is also contemplated that the catalyst for use in the process of this invention may be prepared by forming a promoted metal oxide support in the usual manner hereinbefore set forth, and impregnating the support with an alkali metal which is subsequently aminated or alkali metal amide, and then immersing the impregnated support in liquid ammonia whereby a more uniform distribution of the alkali metal amide over the surface of the promoted metal oxide support is achieved, thereby forming a catalyst which possesses a higher degree of hydrocarbon conversion activity. As hereinbefore set forth, the promoted metal oxide support may be treated with an alkali metal which is subsequently aminated such as potassium, sodium, lithium, cesium or rubidium or the alkali metal amide such as potassium amide, sodium amide, lithium amide, cesium amide and rubidium amide. While the above discussion of the impregnation of the promoted metal oxide support has been concerned principally with an alkali metal which is subsequently aminated it is also contemplated herein that said promoted metal oxide support may also be impregnated with an alkali metal amide by a treatment which is substantially identical with the procedure just described, that is, the promoted metal oxide support is immersed in a liquid ammonia solution of the amide accompanied by vigorous stirring or rotation. The liquid ammonia is allowed to evaporate leaving the desired aminated alkali metal impregnated on the promoted metal oxide support. The liquid ammonia solution of the metal amide may be ~~employed~~ either at or below the atmospheric pressure boiling point of liquid ammonia, namely -33°, or at higher temperatures and correspondingly higher pressures sufficient to maintain the ammonia 130

employed



in liquid phase. For example, the impregnation may be conducted in a pressure autoclave at room temperature, namely at about 20° to 30°C. Upon evaporation of the ammonia, the catalyst may advantageously be treated with an additional amount of gaseous ammonia and then flushed with dried nitrogen, whereupon the catalyst is ready for use in the desired conversion reaction.

10 The process of the present invention may be effected in any suitable manner. One example of a batch type operation which may be used is the conversion of an olefinic hydrocarbon to a polymer thereof. A quantity of the olefinic hydrocarbon, a particular example of which is propylene, is placed in an appropriate apparatus such as a condensation flask or, if high pressures are to be used, in a rotating autoclave. The particular apparatus which has been selected will contain the conversion catalyst of the type described above comprising an aminated alkali metal disposed on a promoted metal oxide support. If so desired a substantially inert inorganic diluent may also be used. Such diluent may be an aromatic hydrocarbon which does not contain an alkyl substituents with α -hydrogen, such as for example benzene, naphthalene, and pyrene or it may be a paraffinic hydrocarbon such as *n*-pentane, *n*-hexane, *n*-heptane, cyclopentane, methylcyclopentane, ethylcyclopentane, and methylcyclohexane. The apparatus and contents thereof are then heated to the desired reaction temperature and maintained thereat for a predetermined period of time. If higher than self-generated pressures are to be used an inert gas such as nitrogen may be pressed into the autoclave until the desired pressure has been reached. At the end of this time the desired reaction product is separated from the catalyst and recovered by fractional distillation, crystallization, or other conventional methods.

45 The process of this invention, however is preferably effected in a continuous type manner since the catalyst comprising an aminated alkali metal disposed on a promoted metal oxide support is particularly suitable for use in a fixed bed type of operation. When this method is used the catalyst is disposed as a fixed bed in a reaction zone maintained at the proper operating conditions while the hydrocarbon reactant and the solvent or diluent, if one is desired, are continuously charged thereto through separate lines. Alternatively, the hydrocarbon reactant and the organic solvent or diluent may be admixed prior to entry into the reactor and charged thereto in a single stream. In carrying out the process of this invention in a continuous manner liquid hourly space velocities (the volume of liquid or liquefied hydrocarbon reactant charged to the reactor per volume of catalyst per hour) may be

varied within a relatively wide range of from about 0.1 to about 20 or more, the preferred range being from about 0.1 to about 10. The desired reaction product is continuously withdrawn from the reaction zone, separated from the reactor effluent and purified by conventional means while the remaining effluent may be recharged at least in part to the reaction zone as a portion of the feed material.

Other continuous types of operations which may be used in this process include the compact moving bed type of operation in which the bed of catalysts and the reactants pass either concurrently or countercurrently to each other in the reaction zone, and the slurry type operation in which the catalyst is carried into the reaction zone as a slurry in one of the reactants.

The process of this invention is preferably effected at an elevated temperature substantially in the range of from 50° to 300°C. Generally speaking the pressure at which this process operates will be dependent upon the particular organic compound or compounds undergoing conversion and the particular catalyst which is used in the process; the pressure should be sufficient to maintain at least a substantial portion of the hydrocarbons in the liquid phase and usually will be in the range of from about 5 to about 250 atmospheres for the condensation reactions.

As hereinbefore set forth, a specific object of this invention is to dimerize propylene to obtain a propylene dimer which may be used as an intermediate in the preparation of isoprene. The isomeric propylene dimer which is best suited for use as an intermediate is 2-methyl-2-pentene which is readily converted to isoprene (2-methyl-1,3-butadiene) by thermal decomposition. In this respect one of the embodiments of the invention particularly suited to obtaining an optimum yield of this desired isomeric dimer of propylene will now be described with reference to the accompanying drawing which is a simplified diagrammatic flow sheet.

In the drawing the unsaturated hydrocarbon feed which, for purposes of illustration, may comprise pure propylene or a propylene-propane mixture recovered from oil refinery operations, is passed through line 1 provided with valve 2 to a first reaction zone or reactor 3 containing a catalyst of the type hereinbefore set forth. This feed, before being passed to the reactor 3 is subjected to a pretreatment which may comprise passing the feed over a material such as molecular sieves to remove any impurities such as nitrogen and/or sulfur, followed by passage over high surface sodium to dry the feed. The reactor effluent is withdrawn through line 4 provided with valves 5 and passed to a first separation zone or depropanizer 6



where unconverted propylene or propylene-propane components, along with any diluent which may be used, are removed overhead through line 7 provided with valve 8. If so desired, the unconverted C_3 components and diluent may be recycled in part, by pumping means not shown, to the reaction zone through line 9 provided with valve 10, the other portion being vented or recovered. The bottoms from depropanizer 6 are withdrawn through line 11 and valve 12 and passed to a second separation zone or deisohexanizer 13. In the second separation zone or deisohexanizer a bottoms product, comprising the desired isomer 2-methyl-2-pentene along with any higher boiling products such as propylene trimer, is separated and this bottoms product is withdrawn through line 17 and valve 18. The low boiling hexene isomers comprising chiefly 2-methyl-1-pentene together with minor quantities of other isomers such as 4-methyl-1-pentene, 3-methyl-1-pentene and 2-ethyl-2-butene, are withdrawn as overhead through line 14 and may be recycled by way of line 26 containing valve 27 to reactor 3 wherein the undesired isomers are isomerized in part to form the desired isomer, that is, 2-methyl-2-pentene. Preferably, however, the product fraction from the top of deisohexanizer 13 is passed through line 14 and valve 15 to a second reaction zone or isomerizer 16. If a second reaction zone is employed the undesired hexene isomers are subjected to isomerization in the presence of a catalyst of the same type as hereinbefore described at a temperature which is lower than that employed in reactor 3, thereby converting the majority of the undesired isomers to the desired isomer, 2-methyl-2-pentene.

The aforesaid isomerization to the desired isomer is due to the fact that the catalysts used in the process of this invention, namely, aminated alkali metal disposed on a promoted metal oxide support, a specific example of which is aminated potassium disposed on a lithiated gamma-alumina support, possess the property of isomerizing propylene dimer so that the double bond of the dimer is shifted to a more centralized position in the chain without further olefin polymerization and without any carbon skeleton rearrangement. The isomerized products are withdrawn from reactor 16 through line 19 provided with valve 20 wherein they are combined with the bottoms from deisohexanizer 13 which had been withdrawn through line 17 and pass out through line 21. The combined products may then be further fractionated, if necessary, in a fractionating zone not shown in the drawing, to separate minor amounts of propylene polymer boiling above the 2-methyl-2-pentene range and also, to separate out any hexene isomers boiling below the 2-methyl-2-pentene range.

If so desired, the latter isomers may then be recycled by means not shown in the drawing to reactor 16 where further isomerization will be completed.

As an alternative method of treating the isomers the bottoms from reactor 16 may be withdrawn through line 19 and passed through line 24 provided with valve 25 into separator 13, thus allowing said separator 13 to act as a common fractionator for both reactor 3 and reactor 16. This will allow recovery of a common product and in addition will provide for recycle of the lower boiling isomers to reactor 16 in the form of overhead from separator 13. It is also contemplated within the scope of this invention that the bottoms from the first separation zone or depropanizer 6 may be passed directly to the second reaction zone or isomerizer 16 wherein isomerization of the undesired isomeric hexenes is accomplished in the presence of the desired hexene isomer, 2-methyl-2-pentene, without further polymerization of the hexenes. By the methods herein shown, the hexene product formed by the dimerization of propylene which normally contains approximately 65% of 2-methyl-2-pentene may be converted to a product containing a substantially greater amount of the desired isomer, that is, said product will contain about 76-78% 2-methyl-2-pentene.

It is also contemplated within the scope of this invention that other olefins may similarly be subjected to double bond isomerization without carbon skeleton rearrangement and with subsequently little or no further polymerization. For example, butene-1 may be isomerized to butene-2, pentene-1 may be isomerized to pentene-2, and 2,3-dimethyl-1-butene may be isomerized to 2,3-dimethyl-2-butene. It is also contemplated within the scope of this invention that, if so desired, the reaction in the first reactor 3 will take place in the presence of organic diluents which are substantially inert in nature, such diluents including paraffinic hydrocarbons such as *n*-pentane, *n*-hexane, and *n*-heptane; or aromatic hydrocarbons which do not have any alkyl substituents which possess an alpha-hydrogen, such as benzene, naphthalene and pyrene. These inert diluents are charged to reactor 3 through line 22 provided with valve 23.

It is to be noted that in the embodiments of the present process described above with reference to the drawing, several steps interact in a uniquely co-operative fashion to obtain the desired result, that is, the recovery of a greater amount of the desired product, such as 2-methyl-2-pentene. For example, in the reaction zone wherein the propylene and/or propylene/propane mixture is dimerized in the presence of a catalyst consisting of an aminated alkali metal disposed



co-operative

on a promoted metal oxide support it has been found essential for prolongation of catalyst activity that a liquid phase be maintained, and for this purpose it is necessary to incorporate in the reaction mixture a relatively high boiling inert diluent, inasmuch as the operating temperature is usually above the critical temperature for propane and propylene. In the mode of operation in which only the reaction zone 3 is used and the low boiling hexenes are recycled to this reaction zone, the recycled hexene act as diluent which facilitates performing the reaction in a liquid phase while at the same time converting the undesired hexene isomers at least partly to the more desirable isomer, 2-methyl-2-pentene, through recirculation of the other isomers to extinction.

It is also contemplated within the scope of this invention that as a variation of the process hereinabove described any propylene trimer and/or higher polymers which have been separated from the 2-methyl-2-pentene fraction may be recycled to the dimerization reaction zone instead of, or together with the lower boiling hexene isomers. In addition to the use of the lower boiling hexene isomers as diluents whereby the dimerization process is effected in a liquid phase it is also contemplated within the scope of this invention that an inert diluent of the group described above may optionally be included in the reaction mixture. The use of such other inert diluents will, of necessity, require additional product fractionation facilities which are unnecessary when the liquid used as a diluent is an internally manufactured fraction. However, an advantage of using such outside diluents will result in a reduction of the amount of hexene recycle with the attendant reduction in the amount of nonenes and higher polymer production through interaction of the recycle liquid and propylene, although the latter occurs in only a relatively minor amount as compared to the desired reaction which is the dimerization of propylene.

As hereinabove mentioned the process of this invention in one of the embodiments thereof involves the copolymerization of olefins containing dissimilar structures or configurations which is effected in the presence of the catalyst prescribed for use in the present process. The reaction conditions under which this copolymerization operates are preferably chosen so that the copolymerization reaction is effected in a substantially liquid phase, so that longer catalyst life and continued high conversion activity are favored. While this copolymerization is generally effected at temperatures substantially in the range of from 75° to 250°C. and at pressures ranging from about 34 to about 136 atmospheres it is advantageously

effected in the presence of a substantially inert diluent of the group of paraffinic and aromatic hydrocarbons already described above, such hydrocarbons including also *n*-octane, *n*-nonane, benzene, and tertalkyl benzenes.

Also the condensation, hereinbefore referred to, of an unsaturated hydrocarbon which does not possess a primary allylic hydrogen atom is preferably effected at temperatures substantially in the range of from 50° to 250° at a pressure in the range of from about 34 to about 170 atmospheres and such that the reactants are maintained substantially completely in liquid phase. In addition, in order to better effect the reaction in a liquid phase thereby prolonging catalyst life and activity, a substantially inert diluent or solvent of the group of inert paraffinic and aromatic hydrocarbons described above will be used in admixture with the unsaturated hydrocarbon reactant. It is also contemplated within the scope of this invention that the diluent which may be used in the polymerization of olefinic hydrocarbon free from a primary allylic hydrogen atom may consist of or contain an undesired isomer of the desired polymerization reaction product, the undesired isomer being separated from the desired isomer in a separation zone and then recycled to the reaction zone. As indicated above, the undesired isomers, beside acting as a diluent when thus recycled, also will undergo isomerization in the presence of the catalyst prescribed for use in the present process.

The following examples are given to illustrate the process of the present invention, but are not intended to unduly limit the scope of the invention.

EXAMPLE I

A support for a catalyst was prepared by calcining approximately 500 cc. of fluoride-free alumina spheres for a period of four hours at 550°C. Following this the spheres were stored in a desiccator. Fifty cc. of these spheres were impregnated with lithium hydroxide solution equal to 0.5 weight percent (calculated as lithium) relative to the alumina, and then calcined for an additional two hours at 550°C.

300 cc. of ammonia gas were condensed in a 500 ml. flask in the presence of 0.2 g. of calcined ferric oxide as a promoter. The flask was maintained at the reflux temperature of ammonia and potassium was slowly added to the flask in small increments. When the reaction of the potassium with the condensed ammonia gas was completed 50 cc. of the promoted support, namely the alumina which had previously been treated with lithium hydroxide were added. After the lithiated alumina was impregnated with potassium amide, the excess ammonia was removed by evaporation from the mixture



while this mixture was continuously stirred. Following the evaporation of the ammonia the catalyst was flushed with dried nitrogen. This catalyst was designated by the letter

5 "A."

A second conversion was prepared in the following manner. Fifty cc. of precalcined fluoride-free alumina spheres were again calcined at a temperature of about 550°C. for a period of two hours and then treated with lithium hydroxide solution equivalent to 0.5 weight percent of lithium, relative to the alumina, following which the material was once more calcined at 550°C. for two hours. A 300 cc. Florence flask which had grooves spirally around the bulb of the glass to improve mixing when rotated and was equipped with a thermometer well was dried at a temperature of approximately 115°C. and flushed with dried nitrogen gas. The lithiated alumina, which was still hot from the calcining, was added to this flask and thoroughly flushed with dried nitrogen, and the flask was then stoppered. The stoppered flask was placed in a rotating device, the stopper was removed and another stopper inserted, the latter stopper being equipped with a stainless steel tube leading from about the middle of the bulb to a swivel. In addition the stopper was also equipped with a small vent tube. Potassium metal which had been stored under pure *n*-heptane was added to this flask and dried nitrogen gas was passed through the swivel and into the rotating flask and out the vent during the addition to the potassium metal to the flask. The flask was then heated until the potassium metal began to melt and until a reaction temperature of approximately 100°C. was obtained. When the reaction was complete the flask was allowed to cool to room temperature and ammonia gas was passed into the flask while rotating and stirring the mixture. Upon completion of the ammonia of the catalyst the flask was flushed with dried nitrogen. This catalyst was designated by the letter "B."

The two catalysts A and B were used individually to polymerize a propylene-butane mixture.

The reactor comprised a stainless steel tube of 1.22 m length and 25.4 mm inner diameter with a spiral preheater of 45.72 cm length. The tube contained a 12.7 cm catalyst bed which contained approximately 50 cc. of catalyst. The tube was filled with catalyst under a nitrogen flow and sealed. Following this the tube was wrapped with heating tapes and insulated. The system was then pressured with dried nitrogen following which the charge stock comprising a mixture of 50% of propylene and 50% of *n*-butane was pumped to the top of the reactor. The polymerization of the propylene was effected at a temperature ranging from about 200° to about 220°C., a pressure of

about 55-60 atmospheres and a liquid hourly space velocity of 2. The discharge from the reactor was passed to a back pressure regulator which reduced the pressure to atmospheric pressure into a heated distilling flask. A cold finger stabilizer separated the liquid from the unreacted gases which were condensed into a series of 2 traps containing a mixture of acetone and solid carbon dioxide, referred to below as "Dry Ice-acetone." Any uncondensed gases which resulted from the polymerization were passed through a wet test meter. The weighed liquid reduct from the stabilizer was added to the Dry Ice-acetone trap and analyzed.

The results of these tests are set forth in Table I below.

Catalyst	A	B	
Weight % Potassium, relative to Promoted Alumina	20	19.5	85
Test Period			90
Temperature, maximum, °C.	1 215	211	
	2 206	206	
	3 205	205	
C ₃ and heavier liquid, % by weight of propylene charge	1 16.0	15.1	95
	2 31.5	24.9	
	3 31.4	16.2	
C ₃ and heavier paraffins, % by weight of total C ₃ & heavier liquid	1 1.5	0.7	100
	2 0.6	0.3	
	3 0.0	0.2	
C ₃ & heavier liquid, % by weight of total C ₃ & heavier liquid	1 34.1	47.6	105
	2 32.3	29.7	
	3 10.2	6.2	
C ₃ olefins, % by weight of total C ₃ & heavier liquid	1 64.4	51.7	110
	2 67.1	70.0	
	3 89.8	93.6	
2-Methyl-2-Pentene, % by weight of total C ₃ olefins	1 52.7	54.7	115
	2 56.8	58.2	
	3 57.9	55.1	
C ₃ Olefins, % by weight of total C ₃ & heavier olefins	1 27.4	31.0	120
	2 26.5	22.8	
	3 9.0	5.8	
Weight-% of Propylene reacted	1 23.8	20.6	
	2 33.8	25.8	125
	3 32.8	17.5	
Propane produced, % by weight of Propylene charge	1 7.9	5.7	
	2 1.0	0.5	130
	3 1.1	0.8	



product



As it will be noted, the polymerized propylene, namely the C₆ and heavier liquid consisted largely of the dimers of propylene; the remainder being predominantly propylene trimers. Furthermore, it is noted that a major portion of the C₆ olefins produced comprised the desired 2-methyl-2-pentene. It will be noted also that catalysts A and B showed sustained activity for selective propylene dimerization.

EXAMPLE II

A catalyst was prepared by treating gamma-alumina spheres, which had first been calcined at 550°C., with a lithium hydroxide solution and then calcining for 2 hours at 550°C., the final promoted gamma-alumina base containing about 0.5% of lithium based on the alumina. The promoted alumina spheres were then impregnated with metallic potassium amide from a solution prepared by dissolving 12 g. of potassium in 350 cc. of liquid ammonia. The alumina spheres were added with continuous stirring and the liquid ammonia was allowed to evaporate. The final catalyst contained approximately 20% potassium (calculated as metal) based on the alumina.

The thus prepared catalyst was placed in a reaction zone and swept with nitrogen which had been dried by passage over high surface sodium followed by a liquid pentane wash to remove any trace of any residual ammonia which might still be present. The reactor tube containing the flushed catalyst was a standard 22.2 mm inner diameter stainless steel tube surrounded by a block furnace provided with heating means in a manner similar to that described in Example I. The propylene charge was passed through a high surface sodium-containing drier operated at room temperature, and was then charged to the reactor tube. The main normal pentane charge was also pumped through a high surface sodium containing drier operated at a temperature of about 200°C. The propylene-*n*-pentane charge passed through the catalyst bed in a down-flow direction while the reactor was maintained at a temperature of about 135° (inlet) to 150°C. (maximum) and at a pressure of about 122 atmospheres. The product was withdrawn and charged to a depropenizing column following which the depropenized product was collected in a receiver maintained at wet ice temperature. The depropenized product comprising isomeric hexenes was analyzed and found to contain about 67% 2-methyl-2-pentene, 15% 2-methyl-1-pentene, 15% 4-methyl-1-pentene and 2% 4-cis-methyl-2-pentene.

The hexenes thus recovered were then charged in continuous flow to a reaction tube comprising a 25.4 mm inner diameter stainless steel tube equipped with a water jacket. The catalyst of the same kind as

described in the first part of the present example was placed in this reaction tube under high surface sodium-dried nitrogen flow. The hexene was contacted with the catalyst in this reactor at a temperature of about 25°C. (room temperature) and a pressure of 2.04 atmospheres. The results of three runs using this procedure are set forth in Table II below.

Table II

Period of Test	1	2	3
Liquid hourly space velocity	4	2	1
<i>Hexene Product Analysis</i>			
4-Methyl-1-pentene	8.2	7.6	7.6
4-Methyl-cis-2-pentene	1.3	1.3	1.3
2,3-Dimethyl-1-butene	1.3	1.3	1.3
2-Methyl-1-pentene	10.5	10.6	11.1
2-Methyl-2-pentene	76.3	75.3	75.7
trans-2-Hexene	1.3	1.5	1.1
3-Methyl-trans-2-pentene	—	0.6	0.4
3-Methyl-cis-2-pentene	0.4	0.6	0.4
2,3-Dimethyl-2-butene	0.8	1.2	1.1

It will be noted from the above table that an increase in the desired hexene isomer, that is, 2-methyl-2-pentene from approximately 67% up to from 75 to 76% was obtained by passing the isomeric hexenes from the dimerization reaction stage over a catalyst similar to that used for the dimerization, thereby causing a rearrangement of the isomers, whereby the double bond was shifted to a more centralized position, with substantially no rearrangement of the carbon skeleton, and the aforesaid isomer was obtained thereby in a greater yield than is obtained by a one-step dimerization process.

A feed stock comprising a propylene-propane (approximately 50-50%) mixture is charged to a reaction zone containing a hydrocarbon conversion catalyst comprising aminated potassium disposed on a gamma-alumina support which has been promoted by the addition of a lithium compound thereto. This catalyst had been prepared by treating gamma-alumina spheres which had been calcined for four hours at 550°C. prior to use, with a lithium nitrate solution, and further calcining the lithium-treated alumina at a temperature of 550°C. for an additional four hours, the final alumina containing about 0.5% of lithium based on the alumina. The promoted alumina spheres were then impregnated with metallic potassium by rotating the potassium and the promoted alumina in a flask at a temperature of about 100°C. When the impregnation of the potassium on the alumina was completed the flask was cooled to room temperature. Following this the catalyst was then immersed in liquid ammonia and the resulting mixture was constantly stirred while allowing the ammonia to evaporate. The product was then treated with an additional amount of gaseous ammonia and flushed with dried



EXAMPLE III

nitrogen.

The reaction zone containing the thus prepared catalyst was swept with nitrogen which had been dried over high surface sodium in order to remove any excess ammonia. Following this the reaction zone was flushed with liquid pentane for about 24 hours at 150°C. The pentane was removed and the charge was fed into the reaction zone at a liquid hourly space velocity of about 2. The reactor was maintained at a temperature of about 95° (inlet) to about 120°C. (maximum) and a pressure of about 75 atmospheres. The percentage of propylene in the feed mixture was maintained at about 15 mole percent maximum. The effluent from the reactor was withdrawn and charged to a depropanizer wherein the unreacted propylene and propane were removed as overhead. Thus separated propylene-propane was recycled back to the reactor while the bottoms were withdrawn from the depropanizer and passed to a deisohexanizer. The lower boiling isomeric hexenes which boil lower than about 65°C. were withdrawn from the top of the deisohexanizer and recycled to the reaction zone wherein these undesired isomeric hexenes acted as a diluent to maintain the reaction mixture in liquid phase, and in addition, were isomerized partly to the desired 2-methylpentene-2. The bottoms from the deisohexanizer comprising that fraction boiling above about 65°C. were withdrawn and passed to a fractionator wherein the cut boiling from about 67-68°C. comprising 2-methyl-2-pentene was separated and recovered as a concentrate containing over 85% 2-methylpentene-2.

EXAMPLE IV

A catalyst was prepared using promoted gamma-alumina spheres which had been obtained in the same manner as described in Example III and contained about 0.5% of lithium based on the alumina. The promoted gamma-alumina spheres were impregnated with metallic potassium by rotating the potassium and the promoted alumina in a Florence flask at a temperature of about 100°C. When the impregnation of the potassium on the alumina was completed the flask was cooled to room temperature. Following this the catalyst was immersed in liquid ammonia and the resulting mixture was constantly stirred while allowing the ammonia to evaporate. The product was

then treated with an additional amount of gaseous ammonia and flushed with dried nitrogen.

The catalyst thus prepared was placed in a reactor which was thereafter flushed with nitrogen to remove any excess ammonia and again flushed with liquid *n*-pentane. A mixture of butene-2 and propylene was charged to the reactor along with normal pentane. The butene-2 was passed over molecular sieves prior to entry into the reactor in order to dry the butene while the propylene was passed over high surface sodium for the same purpose. The reaction zone was maintained at a temperature of about 140-150°C. and a pressure of 136 atmospheres. The propylene was charged to the reactor at a liquid hourly space velocity of 0.59 and the butene-2 was charged at a liquid hourly space velocity of 0.54. The effluent of the reactor was fractionated to separate the unreacted propylene and butene-2 along with *n*-pentane from the reaction product and this reaction product was subjected to analysis with the following results:

Table III

Hours on Stream	10-20	20-30
Temp. °C.		
Block Furnace		
Catalyst	144	143
Inlet	144	143
Maximum	152	153
Outlet	150	149
Charge rates:		
Propylene	14 g./hr.	
Butene-2	19 g./hr.	
<i>n</i> -Pentane	60 g./hr.	
Total Olefins, Percent of Product		
C ₆ =	65.0	65.0
C ₇ =	30.0	30.0
C ₈ =	5.0	5.0
Conversion of Propylene %	70	70
Butylene	26	29

EXAMPE V

In this example a catalyst was used which had been prepared as described in Example IV. A propylene-isobutylene mixture which had previously been dried over high surface sodium was charged to the reaction zone along with normal pentane at a combined liquid hourly space velocity of 2.3. The conditions and results of this experiment are set forth in Table IV below.

Table IV

Period of Test Hours on Stream	1 0-10	2 10-20	3 20-30	4 30-40	5 40-50
Operating Conditions					
5 Pressure, atm.			122		
Temp. °C.					
Block Furnace	134	134	140	143	143
Catalyst					
10 Inlet	134	134	142	144	144
Maximum	139	139	150	151	153
Outlet	139	139	147	150	152
Charge rates:					
Propylene Charge g./hr.			28		
Isobutylene g./hr.			19		
15 n-Pentane g./hr.			90		
Olefins Produced, Percent					
C ₆ =	65	70		75	75
C ₇ =	20	25		20	20
C ₈ =	5	5		5	5
20 C ₉ =	10				

EXAMPLE VI

In this experiment propylene and butene-1 were copolymerized by passing the charge over a catalyst prepared as described in Example IV. The mixture was charged to a reactor which had been treated in a manner similar to that set forth above, namely by flushing with nitrogen and then with *n*-pentane. The reactor was maintained throughout the experiment at a pressure of about 122 atmospheres. The reactor charge mixture of propylene, butene-1 and *n*-pentane

was introduced to the reactor at a liquid hourly space velocity of 3.01, the propylene being charged at a liquid hourly space velocity of 0.28 and the butene at a liquid hourly space velocity of 0.83. The reactor effluent was fractionated and the unreacted propylene and butene-1 were separated along with the *n*-pentane. The olefinic reaction product was subjected to analysis by a mass spectrometer. The results of this experiment are set forth in Table V below.

Table V

Period of Test Hours on Stream	1 0-10	2 10-20	3 20-30	4 30-40	5 40-50	6 50-60
Operating Conditions						
50 Temp. °C.						
Block Furnace	120	120	150			
Catalyst						
Inlet	119	119	149	149	149	149
Maximum	121	121	152	153	152	152
Outlet	121	121	151	152	151	151
55 Charge rates:						
Propylene				14 g./hr.		
Butylene				50 g./hr.		
n-Pentane				120 g./hr.		
60 Total Olefine Composition, %						
C ₆ =		10		10		10
C ₇ =		20		40		30
C ₈ =		70		50		40
C ₉ =						20

65 EXAMPLE VII

In this example the catalyst preparation and test procedure were as described in Example III above. A mixture of ethylene and propylene was charged together with

n-pentane as a diluent to the reactor at a liquid hourly space velocity of 2.76. The results of this test are set forth in Table VI below.

Table VI

Hours on Stream	0.10	Butene-1, g./hr.	35
		<i>n</i> -Pentane, g./hr.	90
		Butene Conversion, %	100
Operating Conditions		Product Composition, %	
Pressure, atm.	136		
5 Temp. °C.		$C_8=$	100 65
Block Furnace	98		
Catalyst			
Inlet	100	The foregoing examples demonstrate an	
Maximum	105	unusual flexibility which distinguishes the	
10 Outlet	103	present process in its ability to produce not	
		only dimers of special value in rubber	
Charge rates:		manufacture but also a considerable variety	
Ethylene	14 g./hr.	of products needed in other industries, such	70
Propylene	20 g./hr.	as, for example, heptenes for use as gasoline	
<i>n</i> -Pentane	114 g./hr.	blending agents by reason of their relatively	
15 Olefins Produced, %		high octane numbers, unsaturated hydrocar-	
$C_3=$	43	bons of 6 or more carbon atoms, including	75
$C_6=$	17	dimers of butene-1 and its higher homo-	
$C_7=$	40	logues with up to 8 or more carbon atoms	
		for use as alkylating agents in the manufac-	
20 It is to be noted from the above Examples		ture of effective surface active agents, and	
III-VI that a catalytic composite of amin-		miscellaneous olefins for use in the produc-	80
ated alkali metal on a promoted metal oxide		tion of amines, epoxides, and solvent	
support, such as for example aminated		alcohols.	
potassium disposed on a lithiated gamma-			
alumina support, not only allows the poly-		WHAT WE CLAIM IS:—	
25 merization of like olefins, but also is active		1. A process for the catalytic conversion	
in catalyzing the copolymerization of olefins		of an olefinic hydrocarbon by a polymeriza-	85
having a dissimilar configuration.		tion, alkylation or isomerization reaction,	
EXAMPLE VIII		characterized in that said olefinic hydro-	
A catalyst was prepared as described in		carbon conversion is catalyzed by an alkali	
30 Example III. The catalyst was placed in a		metal amide comprising a compound of the	
reactor and therein was flushed with nitro-		formula MNH_2 , where M is an alkali metal,	90
gen which had been dried over high surface		N is nitrogen and H is hydrogen disposed	
sodium. Following this the reactor was		on a promoted support consisting essen-	
flushed with liquid <i>n</i> -pentane at a tempera-		tially of a substantially anhydrous metal	
35 ture of about 150°C. The pentane was re-		oxide having a surface area of from 25 to	
moved and a charge consisting of butene-1		500 square meters per gram, said support	95
which had been dried by passage over mole-		having been promoted by compositing a	
cular sieves and <i>n</i> -pentane which had been		small quantity of an alkali metal or an	
dried by passage over high surface sodium		alkaline earth metal or a compound of one	
40 was pressed into the reactor at a liquid		of said metals with said metal oxide prior	
hourly space velocity of about 2. The re-		to the disposal of said alkali metal amide	100
actor was maintained throughout the test at		thereon.	
a pressure of about 122 atmospheres. The		2. Process as claimed in claim 1 charac-	
reactor effluent was fractionated to remove		terized in that the conversion of the olefinic	
45 <i>n</i> -pentane and any lighter materials present.		hydrocarbon is effected in the presence of an	
The reaction product obtained as fraction-		alkali metal amide disposed on promoted	105
ator bottoms was subjected to analysis. The		substantially anhydrous alumina having a	
conditions and results of this experiment are		surface area of from 100 to 300 square	
set forth in Table VII below.		meters per gram, said alumina having been	
50 Table VII		promoted by compositing with an oxide of	
Hours on Stream	20-30	an alkali metal or alkaline earth metal.	110
Operating Conditions		3. Process as claimed in claim 1 or 2	
Pressure, atm.	122	characterized in that the conversion of the	
Temp. °C.		olefinic hydrocarbon is effected in the pre-	
55 Block Furnace	143	sence of sodium- or potassium amide dis-	
Catalyst		posed on a promoted metal oxide support,	115
Inlet	144	said support having been promoted by an	
Maximum	144	oxide of lithium, sodium, potassium,	
Outlet	143	rubidium or cesium.	
60 LHSV	2	4. Process as claimed in claim 3 charac-	
		terized in that the conversion is effected in	120
		the presence of a catalyst which consists	
		essentially of potassium amide disposed on	

Table VI			
Hours on Stream	0.10	Butene-1, g./hr.	35
Operating Conditions		<i>n</i> -Pentane, g./hr.	90
Pressure, atm.	136	Butene Conversion, %	100
5 Temp. °C.		Product Composition, %	
Block Furnace	98	C ₃ =	100 65
Catalyst		The foregoing examples demonstrate an unusual flexibility which distinguishes the present process in its ability to produce not only dimers of special value in rubber manufacture but also a considerable variety of products needed in other industries, such as, for example, heptenes for use as gasoline blending agents by reason of their relatively high octane numbers, unsaturated hydrocarbons of 6 or more carbon atoms, including dimers of butene-1 and its higher homologues with up to 8 or more carbon atoms for use as alkylating agents in the manufacture of effective surface active agents, and miscellaneous olefins for use in the production of amines, epoxides, and solvent alcohols.	
Inlet	100		
Maximum	105		
10 Outlet	103		
Charge rates:			
Ethylene	14 g./hr.		
Propylene	20 g./hr.		
<i>n</i> -Pentane	114 g./hr.		
15 Olefins Produced, %			
C ₃ =	43		
C ₄ =	17		
C ₇ =	40		

It is to be noted from the above Examples III-VI that a catalytic composite of aminated alkali metal on a promoted metal oxide support, such as for example aminated potassium disposed on a lithiated gamma-alumina support, not only allows the polymerization of like olefins, but also is active in catalyzing the copolymerization of olefins having a dissimilar configuration.

EXAMPLE VIII

A catalyst was prepared as described in Example III. The catalyst was placed in a reactor and therein was flushed with nitrogen which had been dried over high surface sodium. Following this the reactor was flushed with liquid *n*-pentane at a temperature of about 150°C. The pentane was removed and a charge consisting of butene-1 which had been dried by passage over molecular sieves and *n*-pentane which had been dried by passage over high surface sodium was pressed into the reactor at a liquid hourly space velocity of about 2. The reactor was maintained throughout the test at a pressure of about 122 atmospheres. The reactor effluent was fractionated to remove *n*-pentane and any lighter materials present. The reaction product obtained as fractionator bottoms was subjected to analysis. The conditions and results of this experiment are set forth in Table VII below.

Table VII			
Hours on Stream	20-30		
Operating Conditions			
Pressure, atm.	122		
Temp. °C.			
55 Block Furnace	143		
Catalyst			
Inlet	144		
Maximum	144		
Outlet	143		
60 LHSV	2		

WHAT WE CLAIM IS:—

1. A process for the catalytic conversion of an olefinic hydrocarbon by a polymerization, alkylation or isomerization reaction, characterized in that said olefinic hydrocarbon conversion is catalyzed by an alkali metal amide comprising a compound of the formula MNH₂ where M is an alkali metal, N is nitrogen and H is hydrogen disposed on a promoted support consisting essentially of a substantially anhydrous metal oxide having a surface area of from 25 to 500 square meters per gram, said support having been promoted by compositing a small quantity of an alkali metal or an alkaline earth metal or a compound of one of said metals with said metal oxide prior to the disposal of said alkali metal amide thereon.

2. Process as claimed in claim 1 characterized in that the conversion of the olefinic hydrocarbon is effected in the presence of an alkali metal amide disposed on promoted substantially anhydrous alumina having a surface area of from 100 to 300 square meters per gram, said alumina having been promoted by compositing with an oxide of an alkali metal or alkaline earth metal.

3. Process as claimed in claim 1 or 2 characterized in that the conversion of the olefinic hydrocarbon is effected in the presence of sodium- or potassium amide disposed on a promoted metal oxide support, said support having been promoted by an oxide of lithium, sodium, potassium, rubidium or cesium.

4. Process as claimed in claim 3 characterized in that the conversion is effected in the presence of a catalyst which consists essentially of potassium amide disposed on



promoted gamma-alumina, said alumina having been promoted by lithium oxide.

5 5. Process as claimed in any of the claims 1 to 4 characterized in that the conversion is effected in the presence of alkali metal amide disposed on a promoted metal oxide support, the catalyst containing alkali metal amide in an amount of from 2 to 20% by weight (calculated as metal) of the support.

10 6. Process as claimed in any of the claims 1 to 5 characterized in that the conversion of the olefinic hydrocarbon is effected in the presence of the alkali metal amide disposed on a promoted metal oxide support at a temperature in the range of from 50° to 300°C. and a pressure in the range of from 5 to 250 atmospheres.

15 7. Process as claimed in any of the claims 1 to 6 characterized in that a mono-olefinic hydrocarbon is subjected to the conversion in the presence of sodium- or potassium amide disposed on a promoted gamma-alumina, said alumina having been promoted by impregnating with a nitrate of an alkali metal and calcining at a temperature in the range of from 500° to 750°C.

20 8. Process as claimed in any of the claims 1 to 7 characterized in that an olefinic hydrocarbon is passed to a first reaction zone and therein is subjected to a polymerization reaction in the presence of alkali metal amide disposed in a promoted metal oxide support, the effluent of the first reaction zone is passed to a first separation zone wherein unreacted olefinic hydrocarbon is removed, the hydrocarbons formed by the condensation reaction are passed from said first separation zone to a second separation zone and therein are separated into desired and undesired isomers, the desired isomeric product is removed from the process, the undesired isomeric product is passed to a second reaction zone and therein is subjected to isomerization in the presence of alkali metal amide disposed on a promoted metal oxide support, and desired isomeric product is recovered from the effluent of the second reaction zone.

25 9. Process as claimed in claim 8 characterized in that the undesired isomeric product is isomerized in the second reaction zone at a temperature which is lower than the temperature maintained in the first reaction zone and in the range of from 0° to 75°C. and at a pressure in the range of from atmospheric to 136 atmospheres.

30 10. Process as claimed in any of the claims 1 to 7 characterized in that an olefinic hydrocarbon is passed to a reaction zone and therein is subjected to a polymerization reaction in the presence of a diluent and alkali metal amide disposed on a promoted metal oxide support, the effluent from said reaction zone is passed to a first separation zone wherein unreacted olefinic hydrocarbon is removed, the hydrocarbons formed by the

polymerization reaction are passed from said first separation zone to a second separation zone and therein the desired hydrocarbon product is separated from a lower boiling undesired product, said desired hydrocarbon product is recovered and said undesired, lower boiling product is recirculated to the reaction zone as diluent.

35 11. Process as claimed in claim 10 characterized in that propylene is dimerized in the reaction zone at a temperature in the range of from 50° to 250°C. and a pressure of from 48 to 136 atmospheres while said propylene and the diluent are maintained substantially in the liquid phase, unreacted propylene is separated from the effluent of the reaction zone in a first separation zone and is returned to the reaction zone, desired propylene dimer including 2-methyl-2-pentane is separated from the propylene-free reaction product in the second separation zone and is removed from the process, and lower boiling propylene dimer is recycled from said second separation zone to the reaction zone.

40 12. Process as claimed in any of the claims 1 to 7 characterized in that a mixture of olefinic hydrocarbons of dissimilar configuration is subjected at a temperature in the range of from 50° to 250°C. and at a pressure in the range of from 34 to 136 atmospheres in the presence of a diluent and an alkali metal amide disposed on a promoted metal oxide support, and a copolymer is recovered from the resultant reaction product.

45 13. Process as claimed in claim 12 wherein heptenes are produced by copolymerizing propylene and butylene in the presence of normal pentane as diluent and in the presence of potassium amide disposed on a promoted gamma-alumina support while the reactants and the diluent are maintained substantially in liquid phase.

50 14. Process as claimed in any of the claims 1 to 7 characterized in that an olefinic hydrocarbon which does not possess a primary allylic hydrogen atom is passed to a reaction zone and subjected therein to a polymerization reaction in the presence of a diluent and alkali metal amide disposed on a promoted metal oxide support at a pressure at which the unsaturated hydrocarbon and diluent are maintained substantially in liquid phase.

55 15. Process as claimed in claim 14 characterized in that butene-1 is dimerized in the presence of normal pentane at a temperature in the range of from 50° to 250°C. and at a pressure of from 34 to 170 atmospheres in the presence of potassium amide supported on promoted gamma-alumina and the resultant octenes are separated from the effluent of the reaction zone by fractionation.

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16. The process for the catalytic conversion of an olefinic hydrocarbon as claimed in claim 1 and substantially as described.

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