

OLEFIN METATHESIS PROCESS AND CATALYST CONTAINING TUNGSTEN FLUORINE BONDS

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Provisional Application No. 61/427,884 which was filed on December 29, 2010, U.S. Provisional Application No. 61/427,893 which was filed on December 29, 2010, U.S. Application No. 13/156,890 which was filed on June 9, 2011 and U.S. Application No. 13/156,918 which was filed on June 9, 2011, the contents of which are here by incorporated in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to a process and catalyst for the metathesis of olefins in general and specifically for the production of propylene from ethylene and butylene.

DESCRIPTION OF RELATED ART

[0003] Propylene demand in the petrochemical industry has grown substantially, largely due to its use as a precursor in the production of polypropylene for packaging materials and other commercial products. Other downstream uses of propylene include the manufacture of acrylonitrile, acrylic acid, acrolein, propylene oxide and glycols, plasticizer oxo alcohols, cumene, isopropyl alcohol, and acetone. Currently, the majority of propylene is produced during the steam cracking or pyrolysis of hydrocarbon feedstocks such as natural gas, petroleum liquids, and carbonaceous materials (e.g., coal, recycled plastics, and organic materials). The major product of steam cracking, however, is generally ethylene and not propylene.

[0004] Steam cracking involves a very complex combination of reaction and gas recovery systems. Feedstock is charged to a thermal cracking zone in the presence of steam at effective conditions to produce a pyrolysis reactor effluent gas mixture. The mixture is then stabilized and separated into purified components through a sequence of cryogenic and conventional fractionation steps. Generally, the product ethylene is recovered as a low boiling fraction, such as an overhead stream, from an ethylene/ethane splitter column requiring a large number of theoretical stages due to the similar relative volatilities of the ethylene and ethane being

separated. Ethylene and propylene yields from steam cracking and other processes may be improved using known methods for the metathesis or disproportionation of C₄ and heavier olefins, in combination with a cracking step in the presence of a zeolitic catalyst, as described, for example, in US 5,026,935 and US 5,026,936. The cracking of olefins in hydrocarbon feedstocks, to produce these lighter olefins from C₄ mixtures obtained in refineries and steam cracking units, is described in US 6,858,133; US 7,087,155; and US 7,375,257.

[0005] Steam cracking, whether or not combined with conventional metathesis and/or olefin cracking steps, does not yield sufficient propylene to satisfy worldwide demand. Other significant sources of propylene are therefore required. These sources include by-products of fluid catalytic cracking (FCC) and resid fluid catalytic cracking (RFCC), normally targeting gasoline production. FCC is described, for example, in US 4,288,688 and elsewhere. A mixed, olefinic C₃/C₄ by-product stream of FCC may be purified in propylene to polymer grade specifications by the separation of C₄ hydrocarbons, propane, ethane, and other compounds.

[0006] Much of the current propylene production is therefore not “on purpose,” but as a by-product of ethylene and gasoline production. This leads to difficulties in coupling propylene production capacity with its demand in the marketplace. Moreover, much of the new steam cracking capacity will be based on using ethane as a feedstock, which typically produces only ethylene as a final product. Although some hydrocarbons heavier than ethylene are present, they are generally not produced in quantities sufficient to allow for their recovery in an economical manner. In view of the current high growth rate of propylene demand, this reduced quantity of co-produced propylene from steam cracking will only serve to accelerate the increase in propylene demand and value in the marketplace.

[0007] A dedicated route to light olefins including propylene is paraffin dehydrogenation, as described in US 3,978,150 and elsewhere. However, the significant capital cost of a propane dehydrogenation plant is normally justified only in cases of large-scale propylene production units (e.g., typically 250,000 metric tons per year or more). The substantial supply of propane feedstock required to maintain this capacity is typically available from propane-rich liquefied petroleum gas (LPG) streams from gas plant sources. Other processes for the targeted production of light olefins involve high severity catalytic cracking of naphtha and

other hydrocarbon fractions. A catalytic naphtha cracking process of commercial importance is described in US 6,867,341.

[0008] More recently, the desire for propylene and other light olefins from alternative, non-petroleum based feeds has led to the use of oxygenates such as alcohols and, more particularly, methanol, ethanol, and higher alcohols or their derivatives. Methanol, in particular, is useful in a methanol-to-olefin (MTO) conversion process described, for example, in US 5,914,433. The yield of light olefins from such processes may be improved using olefin cracking to convert some or all of the C_4^+ product of MTO in an olefin cracking reactor, as described in US 7,268,265. An oxygenate to light olefins conversion process in which the yield of propylene is increased through the use of dimerization of ethylene and metathesis of ethylene and butylene, both products of the conversion process, is described in US 7,586,018.

[0009] Despite the use of various dedicated and non-dedicated routes for generating light olefins industrially, the demand for propylene continues to outpace the capacity of such conventional processes. Moreover, further demand growth for propylene is expected. A need therefore exists for cost-effective methods that can increase propylene yields from both existing refinery hydrocarbons based on crude oil as well as non-petroleum derived feed sources.

SUMMARY OF THE INVENTION

[0010] This invention relates to a process and catalyst for the metathesis of olefins. Accordingly one embodiment of the invention is a catalyst comprising a tungsten metal compound characterized in that it contains at least one tungsten-fluorine bond, the compound dispersed on a refractory oxide support wherein the compound is chemically bonded to the support.

[0011] In a specific embodiment, the tungsten containing compound is selected from the group consisting of WR_4F , $WOFR_3$, $W(NR')FR_3$ and mixtures thereof and where "R" is an organic group which does not have any hydrogen atoms beta to the tungsten.

[0012] In another aspect, this invention relates to a process for the metathesis of olefins using a catalyst comprising a tungsten compound having at least one tungsten-fluorine bond. Accordingly, an embodiment comprises an olefin metathesis process comprising contacting a hydrocarbon feedstock with a catalyst at metathesis conditions to produce an olefin product,

wherein the hydrocarbon feedstock comprises olefins including a first olefin and a second olefin having a carbon number of at least two greater than that of the first olefin, to produce a third olefin having an intermediate carbon number and the catalyst comprises a tungsten metal compound characterized in that it contains at least one tungsten-fluorine bond, the compound dispersed on a refractory oxide support wherein the compound is chemically bonded to the support.

[0013] In a specific embodiment, the first olefin is ethylene, the second olefin is butylene and the third olefin is propylene.

[0014] In a specific embodiment, the tungsten compound is selected from the group consisting of $\text{WOF}(\text{CH}_2\text{CMe}_3)_3$, $\text{W}(\text{NR}')\text{F}(\text{CH}_2\text{CMe}_3)_3$ and mixtures thereof and wherein R' is selected from the group consisting of H, phenyl, 2,6-dimethylphenyl and methyl and the support is silica.

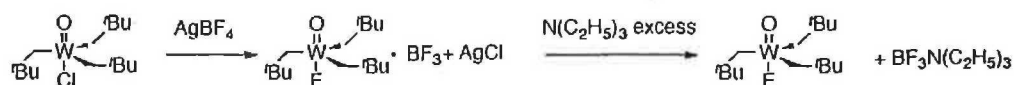
[0015] In another embodiment, the hydrocarbon feedstock is contacted with the catalyst at a temperature from 75°C (167°F) to 400°C (752°F), an absolute pressure from 50 kPa (7.3 psi) to 3,500 kPa (508 psi), and a weight hourly space velocity from 1 to 100 hr^{-1} .

[0016] These and other objects, embodiments and details of this invention will become apparent after a detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

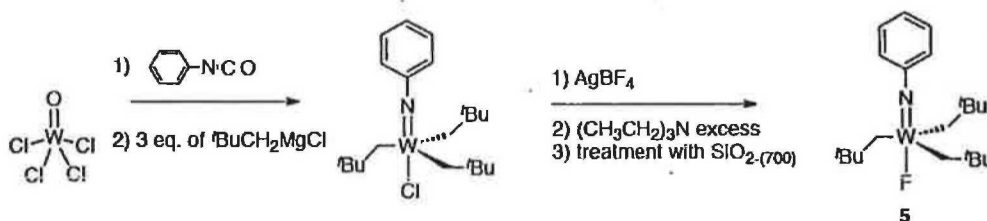
[0017] As stated, this invention relates to a process and catalyst for the metathesis of olefins. The catalyst comprises a tungsten metal compound having at least one tungsten-fluorine bond which is dispersed on a refractory oxide support and the compound is chemically bonded to the support. Accordingly, one necessary component of the invention is a tungsten metal compound with at least one tungsten-fluorine bond. The tungsten metal compound has the empirical formula of: WR_4F , WOFR_3 or $\text{W}(\text{NR}')\text{FR}_3$, wherein R is an organic group which does not have any hydrogen atoms beta to the tungsten, non-limiting examples of which are neopentyl ($-\text{CH}_2\text{CMe}_3$); methyl, 2,2-diethylpropyl ($-\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)_2\text{Me}$), and 2,2-diethylbutyl ($-\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_3$). R' is an organic group such as but not limited to H, phenyl, 2,6-dimethylphenyl, and methyl. The oxo compound can be synthesized by first reacting $\text{O}=\text{WCl}_4$ with an alkylating agent such as RMgCl , RLi , RNa or RK to give $\text{O}=\text{WR}_3\text{Cl}$ which is then reacted with a fluorinating agent such as AgBF_4 , HF or NaF to form the $\text{O}=\text{WR}_3\text{F}$ compound. The reaction product is treated

with a base to remove BF_3 impurities, such as but not limited to NR''_3 wherein non-limiting examples of R'' include H, methyl, ethyl, and phenyl. The overall process can be summarized as follows wherein R is neopentyl and R'' is ethyl.



An alternate way to synthesize the oxo tungsten fluoro compound is to react $(\text{O}=\text{W}-\text{O}-\text{W}=\text{O})\text{R}_6$ with a fluorinating agent (same as above) to produce $\text{O}=\text{WR}_3\text{F}$. Synthesis of $(\text{O}=\text{W}-\text{O}-\text{W}=\text{O})\text{R}_6$ is described in J. AMER. CHEM. SOC., 1983, vol. 105, 7176-7 which is incorporated by reference in its entirety.

[0018] To synthesize the imido compound, often the starting $\text{O}=\text{WCl}_4$ compound is reacted with $\text{R}'\text{isocyanate}$, to yield CO_2 and $\text{R}'\text{N}=\text{WCl}_4$ followed by alkylation and fluorination as above. An example of this synthesis is diagrammatically shown below.



Alternatively, NH_3 can be used in place of R' isocyanate to yield $\text{HN}=\text{WCl}_4$ and H_2O . As shown in the above equation, if all the boron is not removed, it can be removed by treatment with silica.

[0019] Having obtained the tungsten-fluorine bond containing compound, it is now dispersed or grafted onto an inorganic refractory support. Suitable inorganic refractory supports which can be used include, but are not limited to, silica, aluminas, silica-alumina, zirconia, titania, etc. with silica being preferred. Mixtures of refractory oxides can also be used and fall within the bounds of the invention. The support generally has a surface area from 50 to 1000 m^2/g , and preferably from 80 to 500 m^2/g . It should be pointed out that silica-alumina is not a physical mixture of silica and alumina but means an acidic and amorphous material that has been cogelled or coprecipitated. This term is well known in the art, see e.g., US 3,909,450, US 3,274,124 and US 4,988,659, all of which are incorporated by reference in their entirety. Additionally, naturally occurring silica-aluminas such as

attapulgite clay, montmorillonite clay or kieselguhr are within the definition of silica-aluminas.

[0020] Although the supports can be used as powders, it is preferred to form the powder into shaped articles. Examples of shaped articles include but are not limited to spheres, pills, extrudates, irregularly shaped particles and tablets. Methods of forming these various articles are well known in the art. The support can also be in the form of a layer on an inert core such as described in US 6,177,381 which is incorporated by reference in its entirety.

[0021] Spherical particles may be formed, for example, from the preferred alumina by: (1) converting the alumina powder into an alumina sol by reaction with a suitable peptizing acid and water and thereafter dropping a mixture of the resulting sol and a gelling agent into an oil bath to form spherical particles of an alumina gel which are easily converted to a gamma-alumina support by known methods; (2) forming an extrudate from the powder by established methods and thereafter rolling the extrudate particles on a spinning disk until spherical particles are formed which can then be dried and calcined to form the desired particles of spherical support; and (3) wetting the powder with a suitable peptizing agent and thereafter rolling the particles of the powder into spherical masses of the desired size.

[0022] Instead of peptizing an alumina powder, spheres can be prepared as described in US 2,620,314 which is incorporated by reference in its entirety. The first step in this method involves forming an aluminum hydrosol by any of the techniques taught in the art and preferably by reacting aluminum metal with hydrochloric acid. The resultant hydrosol is combined with a suitable gelling agent such as hexamethylene tetraamine (HMT). The resultant mixture is dropped into an oil bath which is maintained at a temperature of 90°C to 100°C. The droplets of the mixture remain in the oil bath until they set and form hydrogel spheres. Next the spheres are continuously withdrawn from the oil bath and treated with an ammoniacal solution at a temperature of 80°C to 95°C for a time of 2 to 2.5 hours. After treatment with the ammoniacal solution, the spheres are dried at a temperature of 80°C to 150°C and then calcined at a temperature of 400°C to 700°C for a time of 1 to 24 hours.

[0023] Extrudates are prepared by mixing the inorganic hydroxide or oxide with water and suitable peptizing agents such as nitric acid, acetic acid, etc. until an extrudable dough is formed. The resulting dough is then extruded through a suitably sized die to form extrudate particles. The extrudate particles are dried at a temperature of 150°C to 200°C and then

calcined at a temperature of 450°C to 800°C for a period of 0.5 to 10 hours to effect the preferred form of the refractory inorganic oxide.

[0024] A preferred support is silica with amorphous silica being one type of silica. Examples include Davisil®646, Davisil®636 (W.R. Grace & Co., Columbia, MD) and other precipitated silicas. Regardless of the source, the silica will have a surface area, either as received or after an optional acid washing step in the catalyst preparation procedure, of at least 50 m²/g and preferably from 80 to 500 m²/g, and most preferably from 400 to 500 m²/g. Another form of silica which can be used is any of the crystalline mesoporous silicas which are defined to be virtually pure silica. These include materials such as MCM-41 and SBA-15. Additional forms of silica are zeolites which are defined to be virtually pure silica. Zeolites are crystalline aluminosilicate compositions which are microporous and which are formed from corner sharing AlO₂ and SiO₂ tetrahedra. By virtually pure silica zeolites is meant that virtually all the aluminum has been removed from the framework. It is well known that it is virtually impossible to remove all the aluminum. Numerically, a zeolite is virtually pure silica when the Si/Al ratio has a value of at least 3,000, preferably 10,000 and most preferably 20,000.

[0025] The silica described above can optionally be acid washed (see US Patent Application No. 12/701,508 which is incorporated by reference in its entirety) to further improve the properties of the resulting catalyst. Acid washing involves contacting the silica with an acid, including an organic acid or an inorganic acid. Particular inorganic acids include nitric acid, sulfuric acid, and hydrochloric acid, with nitric acid and hydrochloric acid being preferred. The acid concentration in aqueous solution, used for the acid washing, is generally in the range from 0.05 molar (M) to 3 M, and often from 0.1 M to 1 M. The acid washing can be performed under static conditions (e.g., batch) or flowing conditions (e.g., once-through, recycle, or with a combined flow of make-up and recycle solution).

[0026] Representative contacting conditions for acid washing the silica support include a temperature generally from 20°C (68°F) to 120°C (248°F), typically from 30°C (86°F) to 100°C (212°F), and often from 50°C (122°F) to 90°C (194°F). The contacting time is generally from 10 minutes to 5 hours, and often from 30 minutes to 3 hours. It has been determined that acid washing increases the BET surface area of the silica support at least 5% (e.g., from 5% to 20%), and often at least 10% (e.g., from 10% to 15%). For zeolitic forms of silica, acid washing decreases the amount of aluminum in the framework, i.e. increases the

Si/Al ratio. A third effect of acid washing is a decrease in the average pore diameter of the silica support. In general, the pore diameter is decreased by at least 5%, and often by at least 10%.

[0027] The tungsten-fluoro compound is now grafted onto the desired support by one of several techniques including contacting the support with a solution containing the tungsten-support, sublimation of the tungsten compound onto the support and direct contacting of the tungsten compound with the desired support. When the tungsten compound is contacted with the support using a solution, the compound is first dissolved in an appropriate solvent. Solvents which can be used to dissolve the compound include but are not limited to diethylether, pentane, benzene, and toluene depending on the R groups and compound reactivity. Contacting is carried out at a temperature of -100° to 80°C, preferably at a temperature of -75° to 35°C for a time of 5 minutes to 24 hours and preferably for a time from 15 minutes to 4 hours. The amount of tungsten-fluoro compound dispersed on the support can vary widely but is usually from 0.5 to 10 wt-% of the catalyst (support plus compound) as the metal. Preferably the amount of compound is from 1.5 to 7 wt-%.

[0028] For sublimation, the tungsten compound is sublimed under dynamic vacuum (typically less than 10^{-3} torr) onto the support by heating the tungsten compound at a temperature of 30°C to 150°C. The support is then heated to a temperature of 30°C to 150°C for 1 to 4 hours, and the excess of the tungsten compound is removed by reverse sublimation at a temperature of 30°C to 150°C and condensed into a cooled area.

[0029] For the direct contact method of grafting the tungsten compound onto the support, the tungsten compound and the support are stirred at a temperature of -10°C to 100°C for a time of 2 to 6 hours under an inert atmosphere, e.g. argon. All volatile compounds are condensed into another reactor. A solvent such as pentane is then introduced into the reactor by distillation, and the solid is washed three times with the solvent e.g. pentane via filtration-condensation cycles. After evaporation of the solvent, the catalyst powder is dried under vacuum. Without being bound by theory, it is thought that regardless of the preparation method, hydroxyls on the support surface react with W-R bond(s) to form W-O-support bonds, with concomitant release of RH.

[0030] The catalyst of the invention is useful as a metathesis catalyst. Olefin metathesis (or disproportionation) processes involve contacting a hydrocarbon feedstock with the catalyst described above at metathesis reaction conditions. The hydrocarbon feedstock refers

to the total, combined feed, including any recycle hydrocarbon streams, to the catalyst in the metathesis reactor or reaction zone, but not including any non-hydrocarbon gaseous diluents (e.g., nitrogen), which may be added along with the feed according to some embodiments. The hydrocarbon feedstock may, but does not necessarily, comprise only hydrocarbons. The hydrocarbon feedstock generally comprises predominantly (i.e., at least 50% by weight) hydrocarbons, typically comprises at least 80% (e.g., from 80% to 100%) hydrocarbons, and often comprises at least 90% (e.g., from 90% to 100% by weight) hydrocarbons.

[0031] Also, in olefin metathesis processes according to the present invention, the hydrocarbons contained in the hydrocarbon feedstock are generally predominantly (i.e., at least 50% by weight, such as from 60% to 100% by weight) olefins, typically they comprise at least 75% (e.g., from 75% to 100%) by weight olefins, and often they comprise at least 85% (e.g., from 85% to 100% or from 95% to 100%) by weight olefins. In other embodiments, these amounts of olefins are representative of the total olefin percentages in the hydrocarbon feedstock itself, rather than the olefin percentages of the hydrocarbons in the hydrocarbon feedstock. In yet further embodiments, these amounts of olefins are representative of the total percentage of two particular olefins in the hydrocarbon feedstock, having differing carbon numbers, which can combine in the metathesis reactor or reaction zone to produce a third olefin having an intermediate carbon number (i.e., having a carbon number intermediate to that of (i) a first olefin (or first olefin reactant) and (ii) a second olefin (or second olefin reactant) having a carbon number of at least two greater than that of the first olefin). In general, the two olefins are present in the hydrocarbon feedstock to the metathesis reactor in a molar ratio of the first olefin to the second olefin from 0.2:1 to 10:1, typically from 0.5:1 to 3:1, and often from 1:1 to 2:1.

[0032] In an exemplary embodiment, the two olefins (first and second olefins) of interest are ethylene (having two carbons) and butylene (having four carbons), which combine in the metathesis reactor or reaction zone to produce desired propylene (having three carbons). The term "butylene" is meant to encompass the various isomers of the C₄ olefin butene, namely butene-1, cis-butene-2, trans-butene-2, and isobutene. In the case of metathesis reactions involving butylene, it is preferred that the butylene comprises predominantly (i.e., greater than 50% by weight) butene-2 (both cis and trans isomers) and typically comprises at least 85% (e.g., from 85% to 100%) butene-2, as butene-2 is generally more selectively converted, relative to butene-1 and isobutylene, to the desired product (e.g., propylene) in the metathesis

reactor or reaction zone. In some cases, it may be desirable to increase the butene-2 content of butylene, for example to achieve these ranges, by subjecting butylene to isomerization to convert butene-1 and isobutylene, contained in the butylene, to additional butene-2. The isomerization may be performed in a reactor that is separate from the reactor used for olefin metathesis. Alternatively, the isomerization may be performed in an isomerization reaction zone in the same reactor that contains an olefin metathesis reaction zone, for example by incorporating an isomerization catalyst upstream of the olefin metathesis catalyst or even by combining the two catalysts in a single catalyst bed. Suitable catalysts for carrying out the desired isomerization to increase the content of butene-2 in the butylene are known in the art and include, for example, magnesium oxide containing isomerization catalysts as described in US 4,217,244.

[0033] As discussed above, the olefins may be derived from petroleum or non-petroleum sources. Crude oil refining operations yielding olefins, and particularly butylene, include hydrocarbon cracking processes carried out in the substantial absence of hydrogen, such as fluid catalytic cracking (FCC) and resid catalytic cracking (RCC). Olefins such as ethylene and butylene are recovered in enriched concentrations from known separations, including fractionation, of the total reactor effluents from these processes. Another significant source of ethylene is steam cracking, as discussed above. A stream enriched in ethylene is generally recovered from an ethylene/ethane splitter as a low boiling fraction, relative to the feed to the splitter, which fractionates at least some of the total effluent from the steam cracker and/or other ethylene containing streams. In the case of olefins derived from non-petroleum sources, both the ethylene and butylene, for example, may be obtained as products of an oxygenate to olefins conversion process, and particularly a methanol to light olefins conversion process. Such processes are known in the art, as discussed above, and optionally include additional conversion steps to increase the butylene yield such as by dimerization of ethylene and/or selective saturation of butadiene, as described in US 7,568,018. According to various embodiments of the invention, therefore, at least a portion of the ethylene in the hydrocarbon feedstock is obtained from a low boiling fraction of an ethylene/ethane splitter and/or at least a portion of the butylene is obtained from an oxygenate to olefins conversion process.

[0034] With respect to the first and second olefins (e.g., ethylene and butylene) that undergo metathesis, the conversion level, based on the amount of carbon in these reactants that are converted to the desired product and by-products (e.g., propylene and heavier, C_5^+

hydrocarbons), is generally from 40% to 80% by weight, and typically from 50% to 75% by weight. Significantly higher conversion levels, on a "per pass" basis through the metathesis reactor or reaction zone, are normally difficult to achieve due to equilibrium limitations, with the maximum conversion depending on the specific olefin reactants and their concentrations as well as process conditions (e.g., temperature).

[0035] In one or more separations (e.g., fractionation) downstream of the metathesis reactor or reaction zone, the desired product (e.g., propylene) may be recovered in substantially pure form by removing and recovering unconverted olefins (e.g., ethylene and butylene) as well as reaction by-products (e.g., C_5^+ hydrocarbons including olefin oligomers and alkylbenzenes). Recycling of the unconverted olefin reactants back to the metathesis reactor or reaction zone may often be desirable for achieving complete or substantially complete overall conversion, or at least significantly higher overall conversion (e.g., from 80% to 100% by weight, or from 95% to 100% by weight) than the equilibrium-limited per pass conversion levels discussed above. The downstream separation(s) are normally carried out to achieve a high purity of the desired product, particularly in the case of propylene. For example, the propylene product typically has a purity of at least 99% by volume, and often at least 99.5% by volume to meet polymer grade specifications. According to other embodiments, the propylene purity may be lower, depending on the end use of this product. For example, a purity of at least 95% (e.g., in the range from 95% to 99%) by volume may be acceptable for a non-polymer technology such as acrylonitrile production, or otherwise for polypropylene production processes that can accommodate a lower purity propylene.

[0036] At the per pass conversion levels discussed above, the selectivity of the converted feedstock olefin components (e.g., ethylene and propylene) to the desired olefin(s) (e.g., propylene) having an intermediate carbon number is generally at least 75% (e.g., in the range from 75% to 100%) by weight, typically at least 80% (e.g., in the range from 80% to 99%) by weight, and often at least 90% (e.g., in the range from 90% to 97%) by weight, based on the amount of carbon in the converted products. The per pass yield of the desired olefin(s) is the product of the selectivity to this/these product(s) and the per pass conversion, which may be within the ranges discussed above. The overall yield, using separation and recycle of the unconverted olefin reactants as discussed above, can approach this/these product selectivity/selectivities, as essentially complete conversion is obtained (minus some purge

and solution losses of feedstock and product(s), as well as losses due to downstream separation inefficiencies).

[0037] The conversion and selectivity values discussed above are achieved by contacting the hydrocarbon feedstock described above, either continuously or batchwise, with a catalyst as described herein. Generally, the contacting is performed with the hydrocarbon feedstock being passed continuously through a fixed bed of the catalyst in an olefin metathesis reactor or reaction zone. For example, a swing bed system may be utilized, in which the flowing hydrocarbon feedstock is periodically re-routed to (i) bypass a bed of catalyst that has become spent or deactivated and (ii) subsequently contact a bed of fresh catalyst. A number of other suitable systems for carrying out the hydrocarbon/feedstock contacting are known in the art, with the optimal choice depending on the particular feedstock, rate of catalyst deactivation, and other factors. Such systems include moving bed systems (e.g., counter-current flow systems, radial flow systems, etc.) and fluidized bed systems, any of which may be integrated with continuous catalyst regeneration, as is known in the art.

[0038] Representative conditions for olefin metathesis (i.e., conditions for contacting the hydrocarbon feedstock and catalyst in the olefin metathesis reactor or reaction zone), in which the above conversion and selectivity levels may be obtained, include a temperature from 75°C (167°F) to 600°C (1112°F), and often from 100°C (212°F) to 500°C (932°F); an absolute pressure from 50 kPa (7.3 psi) to 8,000 kPa (1160 psi), and often from 1,500 kPa (218 psi) to 4,500 KPa (653 psi); and a weight hourly space velocity (WHSV) from 1 hr⁻¹ to 100 hr⁻¹. As is understood in the art, the WHSV is the weight flow of the hydrocarbon feedstock divided by the weight of the catalyst bed and represents the equivalent catalyst bed weights of feed processed every hour. The WHSV is related to the inverse of the reactor residence time. Under the olefin metathesis conditions described above, the hydrocarbon feedstock is normally in the vapor phase in the olefin metathesis reactor or reaction zone, but it may also be in the liquid phase, for example, in the case of heavier (higher carbon number) olefin feedstocks.

[0039] The following examples are set forth to illustrate the invention. It is to be understood that the examples are only by way of illustration and are not intended as an undue limitation on the broad scope of the invention as set forth in the appended claims.

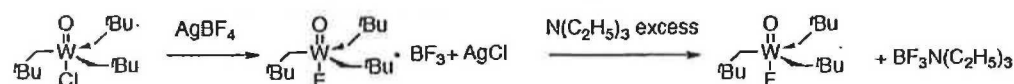
[0040] All experiments were carried out using standard Schlenk and glove-box techniques. Solvents were purified and dried according to standard procedures. SiO₂₋₍₇₀₀₎ was

prepared from AerosilTM silica from Degussa (specific area of 200 m²/g), by partial dehydroxylation at 700°C under high vacuum (10⁻⁵ Torr) for 15 h to give a white solid having a specific surface area of 190 m²/g and containing 0.7 OH nm⁻².

EXAMPLE 1

Synthesis of W=O(CH₂CMe₃)₃

[0041] The synthesis of [W=O(CH₂CMe₃)₃F] was carried out according to the following reaction.

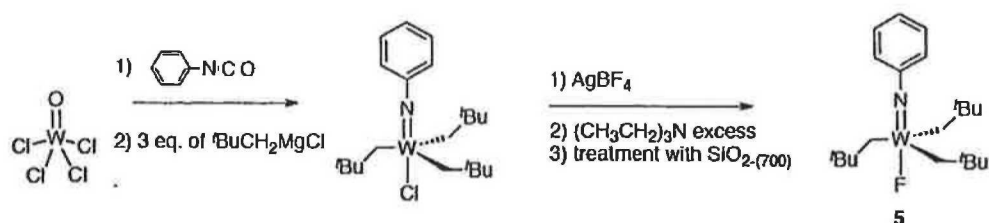


W=O(CH₂CMe₃)₃Cl was synthesized by the literature procedure (Schrock et.al., J. AMER. CHEM. SOC. 1984, 106, 6305-10). [W=O(CH₂CMe₃)₃Cl] (1.5 g,) and AgBF₄ (0.65 g) were stirred in 20 mL of toluene for one hour at room temperature. The reaction mixture was filtered to remove the insoluble AgCl, and NEt₃ (1.1 mL) was added to remove the BF₃ moiety by precipitation as BF₃·N(C₂H₅)₃. The resulting solution was stirred for 16 h at room temperature and then filtered over celite. The solvent was then removed under vacuum to provide a white solid which was sublimed at 60°C under reduced pressure (3.10-5 Torr) to yield 1.13 g of product. The product was analyzed and found to contain 41.47% C; 7.89% H and 4.72% F which agrees well with calculated percentages for C₁₅H₃₃OFW of 41.69% C; 7.69% H and 4.42 % F.

EXAMPLE 2

Synthesis of W(NPh)F(CH₂CMe₃)₃

[0042] W(NPh)F(CH₂CMe₃)₃ was synthesized by reaction of WOCl₄ with C₆H₅NCO, followed by alkylation with neopentyl magnesium chloride as shown below.



Freshly distilled phenylisocyanate (3.214 g) was added to a suspension of $[W=OCl_4]$ (9.000 g) in 200 mL of heptane. This mixture was heated at reflux temperature for 4 days to provide a dark brown precipitate. The solvent was removed under vacuum and Et_2O (20mL) was added resulting in a green solution mixture which was filtered to remove the insoluble impurities and Et_2O was then removed under vacuum producing a powder of dark green crystals of $[W=N(C_6H_5)Cl_4] \cdot (Et_2O)$. A solution of 10.6 g $[W=N(C_6H_5)Cl_4] \cdot (Et_2O)$ in toluene was prepared and stirred rapidly. This solution was cooled to $-78^\circ C$ and to it there were added (dropwise) 30 mL of a 2.17 M ether solution of neopentylmagnesium chloride. The mixture was warmed up slowly to room temperature with continuous stirring at which point the solvent was removed under vacuum. The resulting product was extracted with pentane, and the extract was treated with activated carbon, stirred for 30 minutes, filtered through a bed of celite, and then the solvent was removed under vacuum. The yellow brown residue was collected on a frit, washed with chilled pentane and dried to give 3.8 g of $[W=N(C_6H_5)(CH_2CMe_3)_3Cl]$ as a brown powder.

[0043] A portion of the $[W=N(C_6H_5)(CH_2CMe_3)_3Cl]$ (2.000 g) obtained above and 0.74 g of $AgBF_4$ were stirred in 20 mL of toluene for one hour at room temperature. The reaction mixture was filtered to remove the insoluble $AgCl$, and 1.1 mL of NEt_3 was added. The resulting solution was stirred for 16 h at room temperature, filtered over celite and the solvent then removed under vacuum to provide a yellow pale solid. The product still contained boron as observed by ^{11}B NMR. A solution of the product in pentane was added to $SiO_2-(700)$ (500mg) and reacted for 4 hours. The silica was extracted 3 times with pentane, the solutions combined and the solvent was then removed under vacuum to provide a yellow pale solid. This product was sublimed at $60^\circ C$ under reduced pressure (3×10^{-5} Torr) to yield 580 mg of pure product. The product was analyzed and found to contain 48.86% C; 7.38% H, 4.54% F; 2.74%N and 34.90% W which agrees well with calculated percentages for $C_{21}H_{38}FNW$ of 49.71% C; 7.55% H, 3.74 % F; 2.76%N and 36.23% W.

EXAMPLE 3

Synthesis of $\text{WOF}(\text{CH}_2\text{CMe}_3)_3 / \text{SiO}_2$

[0044] A mixture of the product of Example 1 [$\text{WO}(\text{CH}_2\text{CMe}_3)_3\text{F}$] (500 mg) in pentane (10 mL) and $\text{SiO}_{2-(700)}$ (2 g) was stirred at 25°C overnight. After filtration, the solid was washed 5 times with pentane and all volatile compounds were condensed into another reactor (of known volume) in order to quantify neopentane evolved during grafting. The resulting white powder was dried under vacuum (10^{-5} Torr). Analysis by gas chromatography indicated the formation of 290 μmol of neopentane during the grafting (1.0 ± 0.1 NpH/ W). Elemental analysis showed: W 4.43 wt-%; C 3.27 wt-%.

EXAMPLE 4

Synthesis of $\text{W}(\text{NPh})\text{F}(\text{CH}_2\text{CMe}_3)_3 / \text{SiO}_2$

[0045] A mixture of the product of Example 2 (500 mg), $\text{SiO}_{2-(700)}$ (2 g) and pentane (10 mL) was stirred at 25°C overnight. After filtration, the solid was washed 5 times with pentane. The resulting white powder was dried under vacuum (10^{-5} Torr). Elemental analysis: W 4.8 wt-%; C 6.5 wt-%; N 0.5 wt-%.

EXAMPLE 5

Catalytic testing in propylene metathesis of the catalyst of EXAMPLE 3

[0046] A stainless-steel half-inch cylindrical reactor that can be isolated from ambient atmosphere was charged with 128 mg of the catalyst of Example 3 in a glovebox. After connection to the gas lines and purging of the tubing, a 20 ml/min flow of purified propylene was passed over the catalyst bed at 80°C. Hydrocarbon products were analyzed online by GC. At 30 hours on stream, the catalyst exhibited a total turn over number of 8300. Selectivity was 50% to ethylene and 50% to 2-butenes. The E/Z ratio of the 2-butene formed was 1.5.

EXAMPLE 6

Catalytic testing in propylene metathesis of the catalyst of EXAMPLE 4

[0047] A stainless-steel half-inch cylindrical reactor that can be isolated from ambient atmosphere was charged with 135 mg of the catalyst of Example 4 in a glovebox. After

connection to the gas lines and purging of the tubing, a 20 ml/min flow of purified propylene was passed over the catalyst bed at 80°C. Hydrocarbon products were analyzed online by GC. At 30 hours on stream, the catalyst exhibited a total turn over number of 1150. Selectivity was 50% to ethylene and 50% to 2-butenes. The E/Z ratio of the 2-butene formed was 0.9.

[0048] In an embodiment, the invention is a first catalyst for the metathesis of olefins comprising a tungsten metal compound characterized in that it contains at least one tungsten-fluorine bond, the compound dispersed on a refractory oxide support wherein the compound is chemically bonded to the support. In an embodiment, the invention is a second catalyst according to the first catalyst wherein the tungsten containing compound is selected from the group consisting of WR_4F , $WOFR_3$, $W(NR')FR_3$ and mixtures thereof and where "R" is an organic group which does not have any hydrogen atoms beta to the tungsten.

[0049] In an embodiment, the invention is a third catalyst according to the second catalyst wherein R is selected from the group consisting of neopentyl ($-CH_2CMe_3$); methyl, 2,2-diethylpropyl ($-CH_2C(CH_2CH_3)_2Me$); and 2,2-diethylbutyl ($-CH_2C(CH_2CH_3)_2CH_2CH_3$). In an embodiment, the invention is a fourth catalyst according to the second or third catalyst wherein R' is an organic group selected from the group consisting of H, phenyl, 2,6-dimethylphenyl, and methyl.

[0050] In an embodiment, the invention is a fifth catalyst according to any one of the first, second, third, or fourth catalyst wherein the tungsten is present in an amount from 0.5 to 10 wt-% of the catalyst as the metal. In an embodiment, the invention is a sixth catalyst according to any one of the first, second, third, fourth, or fifth catalyst wherein the refractory oxide support is selected from the group consisting of silica, aluminas, silica-aluminas, titania, zirconia and mixtures thereof. In an embodiment, the invention is a seventh catalyst according to sixth catalyst wherein the refractory oxide is silica. In an embodiment, the invention is an eighth catalyst according to seventh catalyst wherein the silica is an acid washed silica.

[0051] In an embodiment, the invention is a ninth catalyst according to any one of the first, second, third, fourth, fifth, sixth, seventh, or eighth catalyst wherein the refractory oxide support has a surface area of at least 50 m²/g. In an embodiment, the invention is a tenth catalyst according to any one of the first, second, third, fourth, fifth, sixth, seventh, or eighth catalyst wherein the refractory oxide support has a surface area from 80 to 500 m²/g.

[0052] In an embodiment, the invention is a first process for preparing a catalyst for the metathesis of olefins comprising a tungsten metal compound characterized in that it contains at least one tungsten-fluorine bond, the compound dispersed on a refractory oxide support wherein the compound is chemically bonded to the support; the first process comprising contacting the tungsten metal compound with the support by a method selected from the group consisting of: 1) contacting the support with a solution of the compound at solution contacting conditions; 2) subliming the tungsten metal compound onto the support at sublimation conditions and 3) directly contacting the tungsten metal compound with the support at direct contacting conditions.

[0053] In an embodiment, the invention is a second process according to the first process wherein the method of preparation comprises contacting a solution of a tungsten metal compound with a refractory oxide support at a temperature of -100°C to 80°C , for a time of 5 minutes to 24 hours and recovering the resultant catalyst. In an embodiment, the invention is a third process according to the first or second process wherein the solution comprises from 0.5 to 25 wt-% W as the metal.

[0054] In an embodiment, the invention is a fourth process according to the first process wherein the method of preparation comprises sublimation and sublimation conditions comprise subliming the tungsten metal compound onto the support under vacuum at a temperature of 30°C to 150°C for a time of 1 to 4 hours. In an embodiment, the invention is a fifth process according to the fourth process wherein any excess tungsten metal compound is removed from the catalyst by reverse sublimation at a temperature of 30°C to 150°C and condensed.

[0055] In an embodiment, the invention is a sixth process according to the first process wherein the method of preparation is direct contact and direct contact conditions comprise stirring a mixture of the tungsten metal compound with the support at a temperature of -10°C to 100°C for a time of 2 to 6 hours under an inert atmosphere.

[0056] In an embodiment, the invention is a seventh process according to any one of the first, second, third, fourth, fifth, or sixth process wherein the tungsten containing compound is selected from the group consisting of a WR_4F , WOFR_3 or $\text{W}(\text{NR}')\text{FR}_3$ and mixtures thereof where R is an organic group which does not have any hydrogen atoms beta to the tungsten. In an embodiment, the invention is an eighth process according to the seventh process wherein R is selected from the group consisting of neopentyl ($-\text{CH}_2\text{CMe}_3$); methyl, 2,2-

diethylpropyl ($-\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)_2\text{Me}$); and 2,2-diethylbutyl ($-\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_3$). In an embodiment, the invention is a ninth process according to the seventh or eighth process wherein R' is an organic group selected from the group consisting of H, phenyl, 2,6-dimethylphenyl, and methyl.

[0057] In a further embodiment, the invention is a first olefin metathesis process comprising contacting a hydrocarbon feedstock with a catalyst at metathesis conditions to produce an olefin product, wherein the hydrocarbon feedstock comprises olefins including a first olefin and a second olefin having a carbon number of at least two greater than that of the first olefin, to produce a third olefin having an intermediate carbon number and the catalyst comprises a tungsten metal compound characterized in that it contains at least one tungsten-fluorine bond, the compound dispersed on a refractory oxide support wherein the compound is chemically bonded to the support.

[0058] In an embodiment the invention is a second olefin metathesis process according to the first olefin metathesis process wherein the tungsten containing compound is selected from the group consisting of WR_4F , WOFR_3 , $\text{W}(\text{NR}')\text{FR}_3$, and mixtures thereof and wherein R is an organic group which does not have any hydrogen atoms beta to the tungsten. In an embodiment the invention is a third olefin metathesis process according to the second olefin metathesis process wherein R is selected from the group consisting of neopentyl ($-\text{CH}_2\text{CMe}_3$); methyl, 2,2-diethylpropyl ($-\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)_2\text{Me}$); and 2,2-diethylbutyl ($-\text{CH}_2\text{C}(\text{CH}_2\text{CH}_3)_2\text{CH}_2\text{CH}_3$). In an embodiment the invention is a fourth olefin metathesis process according to the second or third olefin metathesis process wherein R' is an organic group selected from the group consisting of H, phenyl, 2,6-dimethylphenyl, and methyl.

[0059] In an embodiment, the invention is a fifth olefin metathesis process according to any one of the first, second, third, or fourth olefin metathesis process wherein the tungsten is present in an amount from 0.5 to 10 wt-% of the catalyst as the metal. In an embodiment, the invention is a sixth olefin metathesis process according to any one of the first, second, third, fourth, or fifth olefin metathesis process wherein the refractory oxide support is selected from the group consisting of silica, aluminas, silica-aluminas, titania, zirconia and mixtures thereof. In an embodiment, the invention is a seventh olefin metathesis process according to sixth olefin metathesis process wherein the refractory oxide is silica. In an embodiment, the invention is an eighth olefin metathesis process according to seventh olefin metathesis process wherein the silica is an acid washed silica.

[0060] In an embodiment, the invention is a ninth olefin metathesis process according to any one of the first, second, third, fourth, fifth, sixth, seventh, or eighth olefin metathesis process wherein the refractory oxide support has a surface area of at least 50 m²/g.

In an embodiment, the invention is a tenth olefin metathesis process according to any one of the first, second, third, fourth, fifth, sixth, seventh, or eighth olefin metathesis process wherein the refractory oxide support has a surface area from 80 to 500 m²/g.

[0061] In an embodiment, the invention is an eleventh olefin metathesis process according to any one of the first, second, third, fourth, fifth, sixth, seventh, eighth, ninth, or tenth olefin metathesis process wherein the olefins are present in an amount of at least 80% by weight of the hydrocarbon feedstock. In an embodiment, the invention is a twelfth olefin metathesis process according to any one of the first, second, third, fourth, fifth, sixth, seventh, eighth, ninth, tenth, or eleventh olefin metathesis process wherein a molar ratio of the first olefin to the second olefin in the hydrocarbon feedstock is from 0.5:1 to 3:1.

[0062] In an embodiment, the invention is a thirteenth olefin metathesis process according to any one of the first, second, third, fourth, fifth, sixth, seventh, eighth, ninth, tenth, eleventh, or twelfth olefin metathesis process wherein the first olefin is ethylene, the second olefin is butylene, and the third olefin is propylene. In an embodiment, the invention is a fourteenth olefin metathesis process according to any one of the first, second, third, fourth, fifth, sixth, seventh, eighth, ninth, tenth, eleventh, twelfth, or thirteenth olefin metathesis process wherein the hydrocarbon feedstock is contacted with the catalyst at a temperature from 75°C (167°F) to 400°C (752°F), an absolute pressure from 0.5 bar (7.3 psi) to 35 bar (508 psi), and a weight hourly space velocity from 1 to 100 hr⁻¹. In an embodiment, the invention is a fifteenth olefin metathesis process according to the thirteenth olefin metathesis process wherein a butene feed is isomerized prior to being fed to the catalyst.

[0063] In an embodiment, the invention is a sixteenth olefin metathesis process according to any one of the first, second, third, fourth, fifth, sixth, seventh, eighth, ninth, tenth, eleventh, twelfth, thirteenth, fourteenth, or fifteenth olefin metathesis process wherein selectivity to the third olefin is greater than 75%. In an embodiment, the invention is a seventeenth olefin metathesis process according to any one of the first, second, third, fourth, fifth, sixth, seventh, eighth, ninth, tenth, eleventh, twelfth, thirteenth, fourteenth, fifteenth, or sixteenth olefin metathesis process wherein selectivity to the third olefin is at least 90%.

[0064] In an embodiment, the invention is an eighteenth olefin metathesis process according to the thirteenth olefin metathesis process wherein the unconverted ethylene and butene are separated from the third olefin propylene and recycled as feed to the process. In an embodiment, the invention is a nineteenth olefin metathesis process according to the thirteenth olefin metathesis process wherein at least a portion of the ethylene in the hydrocarbon feedstock is obtained from a low boiling fraction of an ethylene/ethane splitter, or at least a portion of the butylene is obtained from an oxygenate to olefins conversion process, or at least a portion of the ethylene in the hydrocarbon feedstock is obtained from a low boiling fraction of an ethylene/ethane splitter and at least a portion of the butylene is obtained from an oxygenate to olefins conversion process.

CLAIMS:

1. A catalyst for the metathesis of olefins comprising a tungsten metal compound characterized in that it contains at least one tungsten-fluorine bond, the compound dispersed on a refractory oxide support wherein the compound is chemically bonded to the support.
2. The catalyst of claim 1 where the tungsten containing compound is selected from the group consisting of WR_4F , $WOFR_3$, $W(NR')FR_3$ and mixtures thereof and where "R" is an organic group which does not have any hydrogen atoms beta to the tungsten.
3. The catalyst of claim 2 where R is selected from the group consisting of neopentyl ($-CH_2CMe_3$); methyl, 2,2-diethylpropyl ($-CH_2C(CH_2CH_3)_2Me$), and 2,2-diethylbutyl ($-CH_2C(CH_2CH_3)_2CH_2CH_3$).
4. The catalyst of claim 2 or 3 where R' is an organic group selected from the group consisting of H, phenyl, 2,6-dimethylphenyl and methyl.
5. The catalyst of claim 1 where the tungsten is present in an amount from 0.5 to 10 wt-% of the catalyst as the metal.
6. A process for preparing a catalyst for the metathesis of olefins comprising a tungsten metal compound characterized in that it contains at least one tungsten-fluorine bond, the compound dispersed on a refractory oxide support wherein the compound is chemically bonded to the support; the process comprising contacting the tungsten metal compound with the support by a method selected from the group consisting of: 1) contacting the support with a solution of the compound at solution contacting conditions; 2) subliming the tungsten metal compound onto the support at sublimation conditions and 3) directly contacting the tungsten metal compound with the support at direct contacting conditions.
7. An olefin metathesis process comprising contacting a hydrocarbon feedstock with a catalyst at metathesis conditions to produce an olefin product, wherein the hydrocarbon feedstock comprises olefins including a first olefin and a second olefin having a carbon number of at least two greater than that of the first olefin, to produce a third olefin having an intermediate carbon number and the catalyst comprises a tungsten metal compound characterized in that it contains at least one tungsten-fluorine bond, the compound dispersed on a refractory oxide support wherein the compound is chemically bonded to the support.

8. The process of claim 7 wherein a molar ratio of the first olefin to the second olefin in the hydrocarbon feedstock is from 0.5:1 to 3:1.
9. The process of claim 7 wherein the first olefin is ethylene, the second olefin is butylene, and the third olefin is propylene.
10. The process of claim 9 wherein at least a portion of the ethylene in the hydrocarbon feedstock is obtained from a low boiling fraction of an ethylene/ethane splitter, or at least a portion of the butylene is obtained from an oxygenate to olefins conversion process, or at least a portion of the ethylene in the hydrocarbon feedstock is obtained from a low boiling fraction of an ethylene/ethane splitter and at least a portion of the butylene is obtained from an oxygenate to olefins conversion process.