

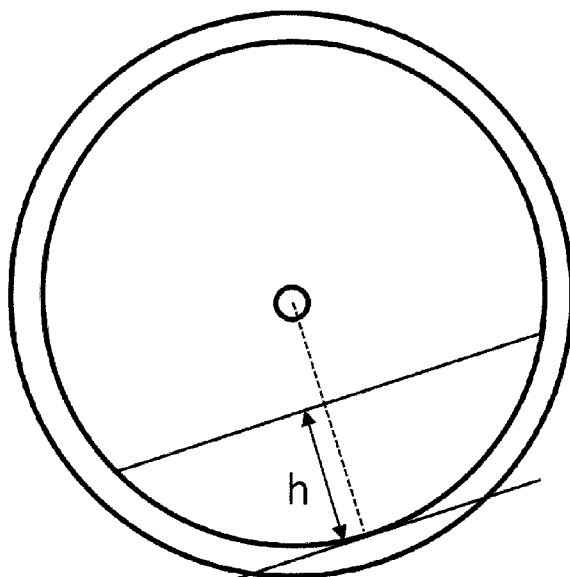


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(54) Title: A METHOD OF PREPARING AN OXYGENATE TO OLEFINS CONVERSION CATALYST AND USE THEREOF

Fig. 1



(57) Abstract: A method of preparing an oxygenate to olefins conversion catalyst comprising: preparing a mixture of a molecular sieve, a binder and optionally clay; forming the mixture into a catalyst precursor; and calcining a bed of the catalyst precursor at a temperature in the range of from 400 °C to 800 °C to form the catalyst wherein the height of the bed of catalyst in the calcination step is at least 2 cm.





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A Method of Preparing an Oxygenate to Olefins Conversion Catalyst and Use Thereof

Field of the Invention

The invention relates to the preparation of an oxygenate to olefins conversion catalyst and its use to convert oxygenates to olefins.

Background

Oxygenate-to-olefin processes are well described in the art. Typically, oxygenate-to-olefin processes are used to produce predominantly ethylene and propylene. An example of such an oxygenate-to-olefin process is described in US Patent Application Publication No. 2011/112344, which is herein incorporated by reference. The publication describes a process for the preparation of an olefin product comprising ethylene and/or propylene, comprising a step of converting an oxygenate feedstock in an oxygenate-to-olefins conversion system, comprising a reaction zone in which an oxygenate feedstock is contacted with an oxygenate conversion catalyst under oxygenate conversion conditions, to obtain a conversion effluent comprising ethylene and/or propylene.

Additional compounds, especially higher molecular weight hydrocarbons are typically produced with the ethylene and propylene in an oxygenate-to-olefins process. A method of improving the yield of lower molecular weight olefins is desired as these olefins, mainly ethylene and propylene, serve as feeds for the production of numerous chemicals. The catalyst and the activity of the catalyst are important to the performance of the reaction step.

Summary of the Invention

The invention provides a method of preparing an oxygenate to olefins conversion catalyst comprising: preparing a mixture of a molecular sieve, a binder and optionally clay; forming the mixture into a catalyst precursor; and calcining a bed of the catalyst precursor at

a temperature in the range of from 400 °C to 800 °C to form the catalyst wherein the height of the bed of catalyst in the calcination step is at least 2 cm.

The invention further provides a process for converting an oxygenate comprising feedstock comprising: feeding an oxygenate comprising feedstock into a reactor containing an oxygenate to olefins conversion catalyst; contacting the feedstock with the catalyst at oxygenate conversion conditions to produce olefins; and removing the olefins from the reactor and further processing the olefins wherein the oxygenate to olefins conversion catalyst was prepared by calcining in a bed of catalyst with a height of at least 2 cm.

Brief Description of the Drawings

Figure 1 depicts an embodiment of the invention using a rotary calciner showing how the height of the catalyst bed is measured

Figure 2 depicts the performance of different catalysts described in the Examples

Detailed Description

The catalyst and method of making the catalyst described herein provides an improved catalyst for the conversion of oxygenates to olefins. This catalyst is effective in any known oxygenate to olefin process, including processes known as methanol to olefins (MTO) and methanol to propylene (MTP). The oxygenate to olefins process can, in certain embodiments, be as described in any of the following references: US 2005/0038304, WO 2006/020083, WO 2007/135052, WO 2009/065848, WO 2009/065877, WO 2009/065875, WO 2009/065870, WO 2009/065855.

The oxygenate to olefins process receives as a feedstock a stream comprising one or more oxygenates. An oxygenate is an organic compound that contains at least one oxygen atom. The oxygenate is preferably one or more alcohols, preferably aliphatic alcohols where the aliphatic moiety has from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, more preferably from 1 to 5 carbon atoms and most preferably from 1 to 4 carbon atoms.

The alcohols that can be used as a feed to this process include lower straight and branched chain aliphatic alcohols. In addition, ethers and other oxygen containing organic molecules can be used. Suitable examples of oxygenates include methanol, ethanol, n-propanol, isopropanol, methyl ethyl ether, dimethyl ether, diethyl ether, di-isopropyl ether, formaldehyde, dimethyl carbonate, dimethyl ketone, acetic acid and mixtures thereof. In a preferred embodiment, the feedstock comprises one or more of methanol, ethanol, dimethyl ether, diethyl ether or a combination thereof, more preferably methanol or dimethyl ether and most preferably methanol.

The oxygenate to olefins process may, in certain embodiments, also receive an olefin co-feed. This co-feed may comprise olefins having carbon numbers of from 1 to 8, preferably from 3 to 6 and more preferably 4 or 5. Examples of suitable olefin co-feeds include butene, pentene and hexene.

Preferably, the oxygenate feed comprises one or more oxygenates and olefins, more preferably oxygenates and olefins in an oxygenate:olefin molar ratio in the range of from 1000:1 to 1:1, preferably 100:1 to 1:1. More preferably, in a oxygenate:olefin molar ratio in the range of from 20:1 to 1:1, more preferably in the range of 18:1 to 1:1, still more preferably in the range of 15:1 to 1:1, even still more preferably in the range of 13:1 to 1:1. It is preferred to convert a C4 olefin, including recycled C4 olefins, together with an oxygenate, to obtain a high yield of ethylene and propylene, therefore preferably at least one mole of oxygenate is provided for every mole of C4 olefin.

The olefin co-feed may also comprise paraffins. These paraffins may serve as diluents or in some cases they may participate in one or more of the reactions taking place in the presence of the catalyst. The paraffins may include alkanes having carbon numbers from 1 to 10, preferably from 3 to 6 and more preferably 4 or 5. The paraffins may be recycled from separation steps occurring downstream of the oxygenate to olefins conversion step.

The oxygenate to olefins process may, in certain embodiments, also receive a diluent co-feed to reduce the concentration of the oxygenates in the feed to suppress side reactions that lead primarily to high molecular weight products. The diluent should generally be non-reactive to the oxygenate feedstock or to the catalyst. Possible diluents include helium, argon, nitrogen, carbon monoxide, carbon dioxide, water and mixtures thereof. The more preferred diluents are water and nitrogen with the most preferred being water.

The diluent may be used in either liquid or vapor form. The diluent may be added to the feedstock before or at the time of entering the reactor or added separately to the reactor or added with the catalyst. In one embodiment, the diluents is added in an amount in the range of from 1 to 90 mole percent, more preferably from 1 to 80 mole percent, more preferably from 5 to 50 mole percent, most preferably from 5 to 40 mole percent.

During the conversion of the oxygenates in the oxygenate to olefins conversion reactor, steam is produced as a by-product, which serves as an in-situ produced diluent. Typically, additional steam is added as diluent. The amount of additional diluent that needs to be added depends on the in-situ water make, which in turn depends on the composition of the oxygenate feed. Where the diluent provided to the reactor is water or steam, the molar ratio of oxygenate to diluent is between 10:1 and 1:20.

The oxygenate feed is contacted with the catalyst at a temperature in the range of from 200 to 1000 °C, preferably of from 300 to 800 °C, more preferably of from 350 to 700 °C, even more preferably of from 450 to 650°C. The feed may be contacted with the catalyst at a temperature in the range of from 530 to 620 °C or from 580 to 610 °C. The feed may be contacted with the catalyst at a pressure in the range of from 0.1 kPa (1 mbar) to 5 MPa (50 bar), preferably of from 100 kPa (1 bar) to 1.5 MPa (15 bar), more preferably of from 100 kPa (1 bar) to 300 kPa (3 bar). Reference herein to pressures is to absolute pressures.

A wide range of WHSV for the feedstock may be used. WHSV is defined as the mass of the feed (excluding diluents) per hour per mass of catalyst. The WHSV should preferably be in the range of from 1 hr⁻¹ to 5000 hr⁻¹.

The process takes place in a reactor and the catalyst may be present in the form of a fixed bed, a moving bed, a fluidized bed, a dense fluidized bed, a fast or turbulent fluidized bed, a circulating fluidized bed; or riser reactors, hybrid reactors or other reactor types known to those skilled in the art may be used. In one embodiment, the reactor is a riser reactor. The advantage of a riser reactor is that it allows for very accurate control of the contact time of the feed with the catalyst, as riser reactors exhibit a flow of catalyst and reactants through the reactor that approaches plug flow.

The feedstocks described above are converted primarily into olefins. The olefins produced from the feedstock typically have from 2 to 30 carbon atoms, preferably from 2 to 8 carbon atoms, more preferably from 2 to 6 carbon atoms, most preferably ethylene and/or propylene. In addition to these olefins, diolefins having from 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins may be produced in the reaction.

In a preferred embodiment, the feedstock, preferably one or more oxygenates, is converted in the presence of a molecular sieve catalyst into olefins having from 2 to 6 carbon atoms. Preferably the oxygenate is methanol, and the olefins are ethylene and/or propylene.

The products from the reactor are typically separated and/or purified to prepare separate product streams in a recovery system. Such systems typically comprise one or more separation, fractionation or distillation towers, columns, and splitters and other associated equipment, for example, various condensers, heat exchangers, refrigeration systems or chill trains, compressors, knock-out drums or pots, pumps and the like.

The recovery system may include a demethanizer, a deethanizer, a depropanizer, a wash tower often referred to as a caustic wash tower and/or quench tower, absorbers, adsorbers, membranes, an ethylene-ethane splitter, a propylene-propane splitter, a butene-butane splitter and the like.

Typically in the recovery system, additional products, by-products and/or contaminants may be formed along with the preferred olefin products. The preferred products, ethylene and propylene are preferably separated and purified for use in derivative processes such as polymerization processes.

In addition to the propylene and ethylene, the products may comprise C₄+ olefins, paraffins and aromatics that may be further reacted, recycled or otherwise further treated to increase the yield of the desired products and/or other valuable products. C₄+ olefins may be recycled to the oxygenate to olefins conversion reaction or fed to a separate reactor for cracking. The paraffins may also be cracked in a separate reactor, and/or removed from the system to be used elsewhere or possibly as fuel.

Although less desired, the product will typically comprise some aromatic compounds such as benzene, toluene and xylenes. Although it is not the primary aim of the process, xylenes can be seen as a valuable product. Xylenes may be formed in the OTO process by the alkylation of benzene and, in particular, toluene with oxygenates such as methanol. Therefore, in a preferred embodiment, a separate fraction comprising aromatics, in particular benzene, toluene and xylenes is separated from the gaseous product and at least in part recycled to the oxygenate to olefins conversion reactor as part of the oxygenate feed. Preferably, part or all of the xylenes in the fraction comprising aromatics are withdrawn from the process as a product prior to recycling the fraction comprising aromatics to the oxygenate to olefins conversion reactor.

Catalysts suitable for use in the conversion of oxygenates to olefins may be made from practically any small or medium pore molecular sieve. One example of a suitable type of molecular sieve is a zeolite. Suitable zeolites include, but are not limited to AEI, AEL, AFT, AFO, APC, ATN, ATT, ATV, AWW, BIK, CAS, CHA, CHI, DAC, DDR, EDI, ERI, EUO, FER, GOO, HEU, KFI, LEV, LOV, LTA, MFI, MEL, MON, MTT, MTW, PAU, PHI, RHO, ROG, THO, TON and substituted forms of these types. Suitable catalysts include those containing a zeolite of the ZSM group, in particular of the MFI type, such as ZSM-5, the MTT type, such as ZSM-23, the TON type, such as ZSM-22, the MEL type, such as ZSM-11, and the FER type. Other suitable zeolites are for example zeolites of the STF-type, such as SSZ-35, the SFF type, such as SSZ-44 and the EU-2 type, such as ZSM-48. Preferred zeolites for this process include ZSM-5, ZSM-22 and ZSM-23.

A suitable molecular sieve catalyst may have a silica-to-alumina ratio (SAR) of less than 280, preferably less than 200 and more preferably less than 100. The SAR may be in the range of from 10 to 280, preferably from 15 to 200 and more preferably from 20 to 100.

A preferred MFI-type zeolite for the oxygenate to olefins conversion catalyst has a silica-to-alumina ratio, SAR, of at least 60, preferably at least 80. More preferred MFI-type zeolite has a silica-to-alumina ratio, SAR, in the range of 60 to 150, preferably in the range of 80 to 100.

The zeolite-comprising catalyst may comprise more than one zeolite. In that case it is preferred that the catalyst comprises at least a more-dimensional zeolite, in particular of the MFI type, more in particular ZSM-5, or of the MEL type, such as zeolite ZSM-11, and a one-dimensional zeolite having 10-membered ring channels, such as of the MTT and/or TON type.

It is preferred that zeolites in the hydrogen form are used in the zeolite-comprising catalyst, e.g., HZSM-5, HZSM-11, and HZSM-22, HZSM-23. Preferably at least 50wt%,

more preferably at least 90wt%, still more preferably at least 95wt% and most preferably 100wt% of the total amount of zeolite used is in the hydrogen form. It is well known in the art how to produce such zeolites in the hydrogen form.

Another example of suitable molecular sieves is siliocoaluminophosphates (SAPOs). SAPOs have a three dimensional microporous crystal framework of PO_2^+ , AlO_2^- , and SiO_2 tetrahedral units. Suitable SAPOs include SAPO-17, -18, 34, -35, -44, but also SAPO-5, -8, -11, -20, -31, -36, 37, -40, -41, -42, -47 and -56; aluminophosphates (AlPO) and metal substituted (silico)aluminophosphates (MeAlPO), wherein the Me in MeAlPO refers to a substituted metal atom, including metal selected from one of Group IA, IIA, IB, IIIB, IVB, VB, VIB, VIIIB, VIIIIB and lanthanides of the Periodic Table of Elements. Preferred SAPOs for this process include SAPO-34, SAPO-17 and SAPO-18. Preferred substituent metals for the MeAlPO include Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr.

The molecular sieves described above are formulated into molecular sieve catalyst compositions for use in the oxygenates to olefins conversion reaction. The molecular sieves are formulated into catalysts by combining the molecular sieve with a binder and/or matrix material and/or filler and forming the composition into particles by techniques such as spray-drying, pelletizing, or extrusion. The molecular sieve may be further processed before being combined with the binder and/or matrix. For example, the molecular sieve may be milled and/or calcined.

Suitable binders for use in these molecular sieve catalyst compositions include various types of aluminas, aluminophosphates, silicas and/or other inorganic oxide sol. The binder acts like glue binding the molecular sieves and other materials together, particularly after thermal treatment. Various compounds may be added to stabilize the binder to allow processing.

Matrix materials are usually effective at among other benefits, increasing the density of the catalyst composition and increasing catalyst strength (crush strength and/or attrition resistance). Suitable matrix materials include one or more of the following: rare earth metals, metal oxides including titania, zirconia, magnesia, thoria, beryllia, quartz, silica or sols, and mixtures thereof, for example, silica-magnesia, silica-zirconia, silica-titania, and silica-alumina. In one embodiment, matrix materials are natural clays, for example, kaolin. A preferred matrix material is kaolin.

In one embodiment, the molecular sieve, binder and matrix material are combined in the presence of a liquid to form a molecular sieve catalyst slurry. The amount of binder is in the range of from 2 to 40 wt%, preferably in the range of from 10 to 35 wt%, more preferably in the range of from 15 to 30 wt%, based on the total weight of the molecular sieve, binder and matrix material, excluding liquid (after calcination).

After forming the slurry, the slurry may be mixed, preferably with rigorous mixing to form a substantially homogeneous mixture. Suitable liquids include one or more of water, alcohols, ketones, aldehydes and/or esters. Water is the preferred liquid. In one embodiment, the mixture is colloid-milled for a period of time sufficient to produce the desired texture, particle size or particle size distribution.

The molecular sieve, matrix and optional binder can be in the same or different liquids and are combined in any order together, simultaneously, sequentially or a combination thereof. In a preferred embodiment, water is the only liquid used.

In a preferred embodiment, the slurry is mixed or milled to achieve a uniform slurry of sub-particles that is then fed to a forming unit. A slurry of the zeolite may be prepared and then milled before combining with the binder and/or matrix. In a preferred embodiment, the forming unit is a spray dryer. The forming unit is typically operated at a temperature high enough to remove most of the liquid from the slurry and from the resulting molecular sieve

catalyst composition. In a preferred embodiment, the particles are then exposed to ion-exchange using an ammonium nitrate or other appropriate solution.

In one embodiment, the ion exchange is carried out before the phosphorous impregnation. The ammonium nitrate is used to ion exchange the zeolite to remove alkali ions. The zeolite can be impregnated with phosphorous using phosphoric acid followed by a thermal treatment to H⁺ form. In another embodiment, the ion exchange is carried out after the phosphorous impregnation. In this embodiment, alkali phosphates or phosphoric acid may be used to impregnate the zeolite with phosphorous, and then the ammonium nitrate and heat treatment are used to ion exchange and convert the zeolite to the H⁺ form.

In a preferred embodiment, the zeolite is prepared and made into a slurry. The zeolite is then spray dried to form particles. The particles are dried and then impregnated with a phosphorous containing compound. The catalyst precursor is then dried and calcined.

Alternatively to spray drying the catalyst may be formed into spheres, tablets, rings, extrudates or any other shape known to one of ordinary skill in the art. The catalyst may be extruded into various shapes, including cylinders and trilobes.

The average particle size is in the range of from 1-200 μm , preferably from 50-100 μm . If extrudates are formed, then the average size is in the range of from 1 mm to 10 mm, preferably from 1.5 mm to 7 mm.

The catalyst may further comprise phosphorus as such or in a compound, i.e. phosphorus other than any phosphorus included in the framework of the molecular sieve. It is preferred that a MEL or MFI-type zeolite comprising catalyst additionally comprises phosphorus.

The molecular sieve catalyst is prepared by first forming a molecular sieve catalyst precursor as described above, optionally impregnating the catalyst with a phosphorous

containing compound and then calcining the catalyst precursor to form the catalyst. The phosphorous impregnation may be carried out by any method known to one of skill in the art.

The phosphorus-containing compound preferably comprises a phosphorus species such as PO_4^{3-} , $\text{P}(\text{OCH}_3)_3$, or P_2O_5 , especially PO_4^{3-} . Preferably the phosphorus-containing compound comprises a compound selected from the group consisting of ammonium phosphate, ammonium dihydrogen phosphate, dimethylphosphate, metaphosphoric acid and trimethyl phosphite and phosphoric acid, especially phosphoric acid. The phosphorus containing compound is preferably not a Group II metal phosphate. Group II metal species include magnesium, calcium, strontium and barium; especially calcium.

In one embodiment, phosphorus can be deposited on the catalyst by impregnation using acidic solutions containing phosphoric acid (H_3PO_4). The concentration of the solution can be adjusted to impregnate the desired amount of phosphorus on the precursor. The catalyst precursor may then be dried.

The catalyst precursor, containing phosphorous (either in the framework or impregnated) is calcined to form the catalyst. The calcination of the catalyst is important to determining the performance of the catalyst in the oxygenate to olefins process.

The calcination may be carried out in any type of calciner known to one of ordinary skill in the art. The calcination may be carried out in a tray calciner, a rotary calciner, or a batch oven, optionally in the presence of an inert gas and/or oxygen and/or steam.

The calcination may be carried out at a temperature in the range of from 400 °C to 1000 °C, preferably in a range of from 450 °C to 800 °C, more preferably in a range of from 500 °C to 700 °C. Calcination time is typically dependent on the degree of hardening of the molecular sieve catalyst composition and the temperature and ranges from about 15 minutes to about 2 hours.

In a preferred embodiment, the calcination is carried out in air at a temperature of from 500 °C to 600 °C. The calcination is carried out for a period of time from 30 minutes to 15 hours, preferably from 1 hour to 10 hours, more preferably from 1 hour to 5 hours.

The calcination temperatures described above are temperatures that are reached for at least a portion of the calcination time. For example, in a rotary calciner, there may be separate temperature zones that the catalyst passes through. For example, the first zone may be at a temperature in the range of from 100 to 300 °C. At least one of the zones is at the temperatures specified above. In a stationary calciner, the temperature is increased from ambient to the calcination temperatures above and so the temperature is not at the calcination temperature for the entire time.

The calcination is carried out on a bed of catalyst. For example, if the calcination is carried out in a tray calciner, then the catalyst precursor added to the tray forms a bed which is typically kept stationary during the calcination.

If the calcination is carried out in a rotary calciner, then the catalyst added to the rotary drum forms a bed that although not stationary does maintain some form and shape as it passes through the calciner. This can be more easily seen from Figure 1. Figure 1 shows a cross-sectional view of a rotary calciner where the bed of catalyst has a height h measured at the center of the rotary calciner.

The calcination is carried out so that the bed of catalyst precursor being calcined always has a bed height that is at least 2 cm. The bed height is preferably at least 2.5 cm and more preferably in a range of from 2.5 to 20 cm. The bed height is most preferably in a range of from 2.5 to 15 cm.

Examples

Example 1

In Example 1, five catalyst precursor samples were prepared as follows. ZSM-5 with a SAR (silica-to-alumina) ratio of 80 was used. The ZSM-5 powder was first calcined at 550 °C. Then, the powder was added to an aqueous solution to form a slurry that was then milled. Next, kaolin clay and a silica sol were added and the resulting mixture was spray dried to form particles that had a weight-based average particle size of 70-90 µm. The spray dried catalyst precursors were exposed to ion-exchange using an ammonium nitrate solution. Then phosphorous was deposited on the catalyst precursor by means of impregnation using an acidic solution of phosphoric acid (H₃PO₄). The concentration of the solution was adjusted to impregnate the catalyst with 2.0 wt % of phosphorous on the catalyst. After impregnation the catalysts were dried at 120 °C. The phosphorous loading on the final catalysts is given based on the weight percentage of the elemental phosphorous in any phosphor species, based on the total weight of the formulated catalyst.

Each of the catalyst precursor samples was calcined in a stationary oven at a temperature of 550 °C. The samples were, however, calcined in beds of different heights. Sample A was calcined in a bed with a bed height of 0.5 cm; sample B at a bed height of 1 cm; sample C at a bed height of 2 cm; sample D at a bed height of 3 cm and sample E at a bed height of 5 cm.

Example 2

In Example 2, each of the catalyst samples prepared in Example 1 were tested to determine their performance in conversion of methanol to olefins. The experiments were carried out as follows. A sieve fraction of 40-80 mesh of catalyst was used, which was treated ex-situ in air at 550°C for 2 hours. The catalyst was placed in a quartz reactor tube of 1.8 mm internal diameter. The catalyst was then heated under a flow of nitrogen to the reaction temperature of 525 °C and subsequently the feed composition, comprising 6 vol. % methanol and 3 vol. % C₄ olefins, was passed over the catalyst at atmospheric pressure (1 bar

atmosphere). The gas hourly space velocity (GHSV), i.e. the total gas flow per gram of zeolite per hour, was 48,000 (ml/(g zeolite·hr)). The effluent from the reactor was analyzed by gas chromatography (GC) to determine which products were formed. The combined C2+C3 make is shown in Figure 2. The amount of C2+C3 includes paraffins and olefins.

As can be seen from the examples and Figure 2, the catalysts that were calcined at a bed height of at least 2 cm demonstrated improved C2 and C3 make in the oxygenate to olefins conversion process. The catalyst calcined at bed heights of 3 to 5 cm performed equally well with C2+C3 make of greater than 61 wt%. Catalyst calcined at lower bed heights demonstrated a reduced C2+C3 make in the performance tests to convert methanol to olefins.

Claims

1. A method of preparing an oxygenate to olefins conversion catalyst comprising:
 - a. preparing a mixture of a molecular sieve, a binder and optionally clay;
 - b. forming the mixture into a catalyst precursor; and
 - c. calcining a bed of the catalyst precursor at a temperature in the range of from 400 °C to 800 °C to form the catalystwherein the height of the bed of catalyst in the calcination step is at least 2 cm.
2. The method of claim 1 wherein the calcination step is carried out in a tray calciner and the height of the catalyst bed is the height of catalyst in the tray.
3. The method of claim 1 wherein the calcination step is carried out in a rotary calciner and the height of the catalyst bed is measured as shown in Figure 1.
4. The method of claim 1 wherein the height of the bed of catalyst is in the range of from 2.5 cm to 20 cm.
5. The method of claim 1 wherein the height of the bed of catalyst is at least 3 cm.
6. The method of claim 1 wherein the height of the bed of catalyst is in the range of from 3 to 15 cm.
7. The method of any of claims 1-5 wherein the catalyst is calcined at a temperature in the range of from 500 °C to 600 °C.
8. The method of any of claims 1-6 wherein the forming step comprises spray-drying.
9. The method of any of claims 1-7 wherein the catalyst contains phosphorous.
10. The method of claim 7 wherein the molecular sieve is impregnated with phosphorous before it is mixed with the binder and optionally clay.
11. The method of claim 7 wherein the molecular sieve contains phosphorous in the framework of the molecular sieve.

12. The method of claim 7 wherein the molecular sieve is impregnated with phosphorous after it is formed into a catalyst precursor.
13. A process for converting an oxygenate comprising feedstock comprising:
- a. feeding an oxygenate comprising feedstock into a reactor containing an oxygenate to olefins conversion catalyst;
 - b. contacting the feedstock with the catalyst at oxygenate conversion conditions to produce olefins; and
 - c. removing the olefins from the reactor and further processing the olefins
- wherein the oxygenate to olefins conversion catalyst was prepared by calcining in a bed of catalyst with a height of at least 2 cm.
14. The process of claim 12 wherein the height of the bed of catalyst is in the range of from 2.5 cm to 15 cm.
15. The process of any of claims 12-13 wherein the calcining is carried out in a tray calciner or a rotary calciner.
16. The method of any of claims 12-14 wherein the catalyst was calcined at a temperature in the range of from 500 °C to 600 °C.

Fig. 1

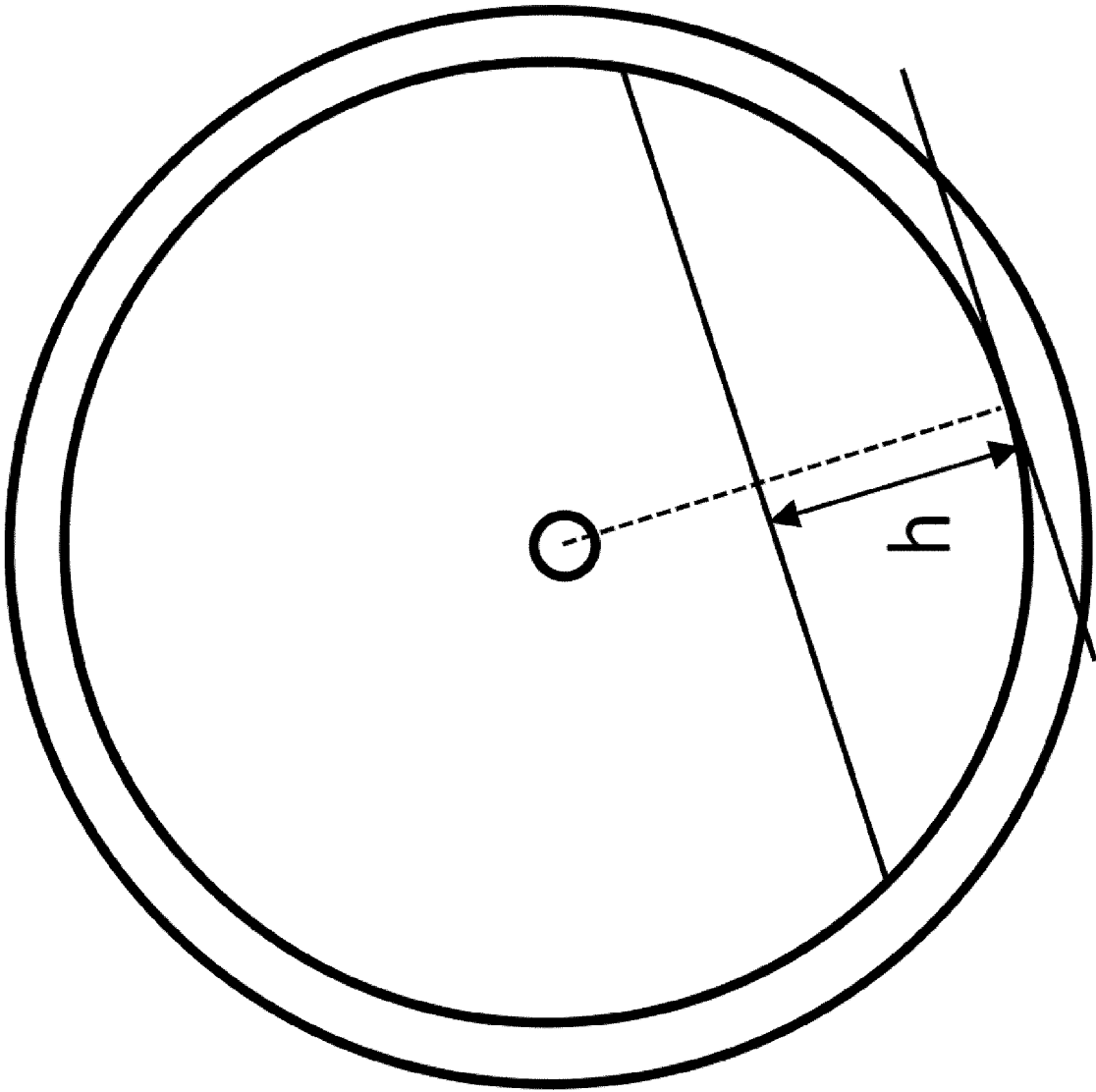
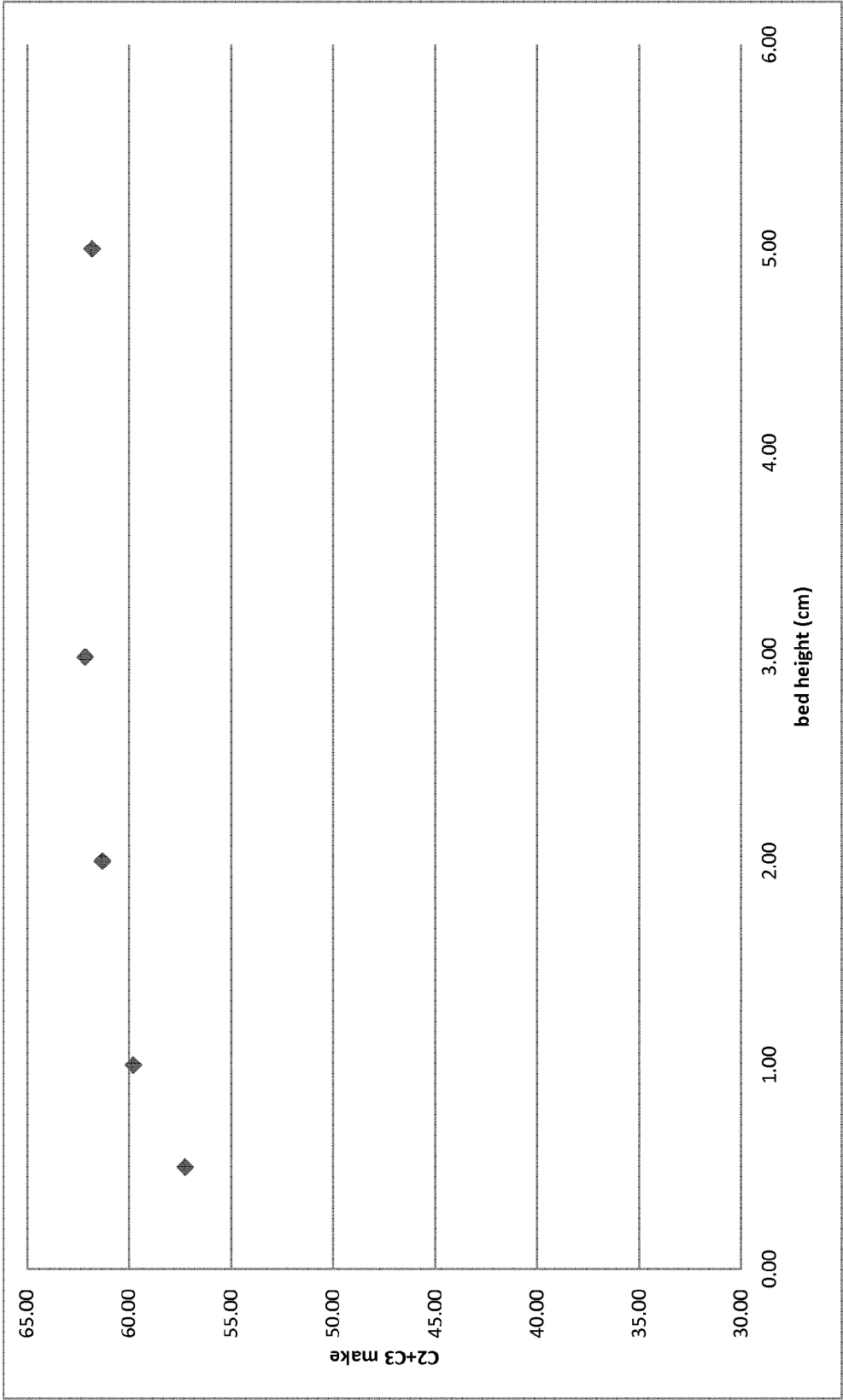


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/063578

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J37/28 B01J37/30 B01J29/40 B01J37/00 C07C1/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 548 644 A1 (RELIANCE IND LTD [IN]) 23 January 2013 (2013-01-23) examples	1-16
X	US 2007/209969 A1 (SHEN BAOJIAN [CN] ET AL) 13 September 2007 (2007-09-13) examples	1-16
X	WO 2011/057980 A1 (SHELL INT RESEARCH [NL]; CHEWTER LESLIE ANDREW [NL]; HENRY HERVE [NL];) 19 May 2011 (2011-05-19) examples	1-16
A	WO 2009/156433 A2 (TOTAL PETROCHEMICALS RES FELUY [BE]; NESTERENKO NIKOLAI [BE]; VERMEIRE) 30 December 2009 (2009-12-30) ----- -/--	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

5 September 2014

Date of mailing of the international search report

19/09/2014

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/063578

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 2 380 663 A1 (MITSUBISHI PLASTICS INC [JP]) 26 October 2011 (2011-10-26) -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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